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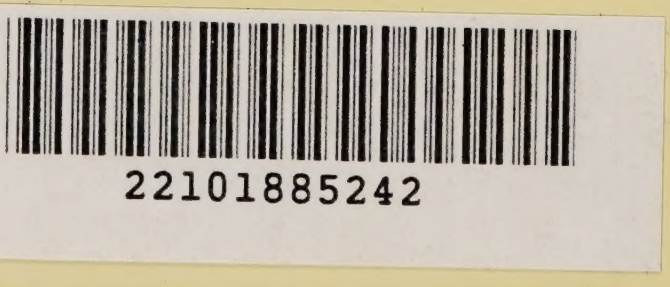

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WATER-ANALYSIS:

A PRACTICAL TREATISE

ON THE

EXAMINATION OF POTABLE WATER.

BY

J. ALFRED WANKLYN

AND

ERNEST THEOPHRON CHAPMAN.

FIFTH EDITION,

BY

J. ALFRED WANKLYN, M.R.C.S.

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WYCOMBE, PETERBOROUGH, AND SHREWSBURY.

LONDON:
TRÜBNER & CO., LUDGATE HILL.
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BALLANTYNE, HANSON AND CO.
EDINBURGH AND LONDON

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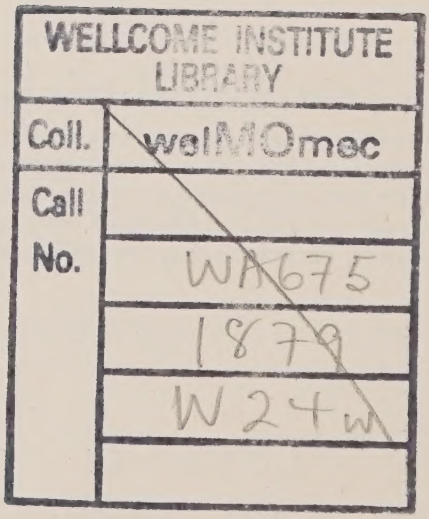

PREFACE TO THE FIFTH EDITION.

NEXT to the confession of my chief adversary, that the ammonia-process of water-analysis is almost universally adopted, I am disposed to place the very favourable reception given to the book which embodies the ammonia-process. Since it came out, in the year 1868, this book has run through four editions, numbering altogether 4000 copies.

In putting forward the fifth edition, I have to announce that it contains a detailed account of the new process of dealing with the organic matter in water which has recently been developed in my laboratory by my friend Mr Cooper and myself.* This process, to which we have given the name, "*the moist combustion process*," is quite as easy of execution as the ammonia-process, and will be found useful in corroboration of the ammonia-process, and in aiding in determining the real character of samples which hitherto have had to be returned as "doubtful." From the comparatively small bulk of the solutions required, and from the smallness of the scale on which it may be worked, it will be found useful to the traveller.

We have adopted the very unusual plan of patenting

* Vide Phil. Mag., June 1878 and Oct. 1878 and Feb. 1879.

our new process, a step which the present condition of the chemical profession in this country renders imperatively necessary. At the same time we desire to say that we have no intention of making an oppressive use of the rights we have acquired: and we shall endeavour to protect the Public against spurious work, as well as to secure for ourselves a fair return for our labours.

In conclusion, I revert to the almost unprecedented success of the Treatise on Water-Analysis, and its companion Treatises, "Milk-Analysis," and "Tea, Coffee, and Cocoa." But success of this description is not without its drawback, and brings the unauthorised imitator on to the stage. In America the Milk-Analysis has been quite simply reprinted; but in this country, where an author has copyright "in literary form and in experimental results"—though not in idea—both the Milk-Analysis and the Water-Analysis have escaped unauthorised reproduction in an unmutilated form, and the unauthorised imitator mutilates and transposes. I here announce that I have authorised no one as my exponent, and I warn all persons interested in sanitary matters against the danger of trusting to the mutilated descriptions of my processes which abound in sanitary literature, and not to distrust them the less though they be highly commended by reviewers.

7 WESTMINSTER CHAMBERS,
LONDON, *May* 1879.

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WATER-ANALYSIS.

INTRODUCTION.

Medical authorities are, at the present time, pretty well agreed that if the water of a well, which has received the excreta of a patient suffering from cholera, or from typhoid fever, be drunk, there is the utmost danger that the drinker may contract those diseases. It is also a received fact that the drinking of water which contains an undue proportion of organic filth—even assuming specific poison to be absent—is injurious to health. Such being the case, the first questions which the sanitarian asks, respecting a given specimen of water which is proposed for use as "potable water," are—Does it contain these septic poisons? Is it abnormally charged with organic filth?

To both these questions the water-analyst is enabled, by the ammonia-process and moist combustion process, to answer, in many instances, by an absolute No. In other cases he can show that the water is abnormally filthy; and, in some cases, that there is danger of specific poison.

In the proper place (Chapter IV.) the ammonia-process will be minutely described and explained. Here, however,

some of the general results which have flowed from the diligent employment of this process during the last seven years may be briefly summarised.

First, it may be mentioned that the ammonia-process is easily able to detect one part of albumen, gelatine, organic alkali, &c., mixed with ten million times its weight of water. Armed with an instrument of this power, my colleagues and myself have proceeded to investigate the condition of natural waters, and have arrived at the following general conclusions :—

There are deep-spring waters—*i.e.*, the water from the Greensand and the Caterham water—which do not contain even this small proportion of nitrogenous organic matter.

So pure (organically considered) are these waters, that it is with difficulty even that the chemist prepares distilled water to vie with them in purity. The water which, after being stored in reservoirs and filtered, is served out by Water Companies to English and Scotch towns, is likewise, as a rule, in a state of high purity. Not indeed to the supreme degree reached by deep springs does the town water-supply attain; but still, whatever the source whence it draws its supply, the town-reservoir discharges surprisingly pure water, if only an honest filtration be performed by the Water Company.

Leaving the pure, deep-spring water, and the fairly pure water of the town water-works, we have found unfiltered river water to be, as might be expected, of variable quality. Sometimes this, too, is fairly pure; but at other times, as when the river Thames has received the Fleet-ditch sewer, it is abominably filthy. The surface-well is most capricious in quality. It may be fairly pure, or it may be disgustingly foul. Of all the kinds of water that are drunk, the dirty

water from the surface-well is the most dangerous. Cholera and typhoid fever may be imbibed along with it; for whilst the water of the well may be dilute urine, or drainage from excrement, the degree of dilution is not necessarily so great as to deprive the poisonous materials of their power.

By the aid of the ammonia-process we are now able to divide potable waters into waters which are clean (*i.e.*, which are devoid of any excess of nitrogenous organic matter); and waters which are dirty (*i.e.*, charged with an abnormal quantity of organic matter).

If a water be dirty, a knowledge of its history, and of course of its mineral constituents, may be of assistance in forming a judgment as to the degree of risk attendant on its employment for domestic use.

In addition to being injurious by reason of organic impurity, water may also be injurious on account of its mineral constituents. These latter may be too excessive in amount, as in the notorious instance of sea-water, or they may be poisonous in themselves. An examination of potable water should therefore include a determination of the amount of inorganic solids in the water, as well as a testing for poisonous metals.

For most sanitary purposes a water-analysis is complete when it includes these data—

Total solids.
Chlorine.
"Free and albuminoid ammonia."
Oxygen consumed in moist combustion.
Poisonous metals.

After giving in Chapter I. a few short directions as to the collection of samples of water, we shall devote a chapter to each of these data in succession; and after that we shall, in

Chapter VII., discuss the drawing up of reports, and the conclusions which follow from the analyses, and with this chapter we close the first part of this treatise.

Part II. is devoted to specialities, and, unlike Part I., is not designed for general reading. The intelligent officer of health will probably only occasionally have need to refer to Part II., which is more especially designed for those who make analytical chemistry a profession. In this part of the book minute directions are given for the making of a complete mineral analysis of a water residue.

When the question is not whether a given sample of water may be drunk with impunity, but whether a given kind of water is desirable for the general supply of a town, then a great many other considerations come into play. With this latter purpose in view, a detailed mineral analysis of the water-residue is essential.

It is desirable that the exact mineral character of each water-supply should be registered, and if that were done, a foundation would be laid for ascertaining the dietetic effects of small quantities of mineral matter.

When called on to advise a township as to its water-supply, the chemist will do well to note the quantity of sulphates and of magnesia in the water, and to reject such waters as contain much of these constituents. Very hard waters, too, should not be generally recommended.

Part III. contains analyses of some natural waters which have been made in my own laboratory, together with some account of those waters.

The Appendix contains original memoirs relating to the ammonia-process, a history and a notice of the controversy concerning water-analysis.

PART I.

WATER-ANALYSIS

FOR

GENERAL SANITARY PURPOSES.

CHAPTER I.

COLLECTION OF SAMPLES OF WATER.

THE quantity of water which the water-analyst should direct to have sent to him for analysis should not be less than half a gallon; unless, indeed, there are difficulties in the way of getting so much. In case of necessity, however, a very small quantity of water may be made to do, if extreme care be taken that the bottle be perfectly clean.

The most convenient kind of bottle for holding the half-gallon of water is the stoppered glass bottle known as the "Winchester Quart," the capacity of which is about half a gallon, and which is to be obtained at most druggists' shops in this country.

Great cleanliness should be insisted upon; and by way of ensuring this, the direction may be given to pour into the bottle a little strong sulphuric acid, and allow it to flow over the inner surface of the bottle, and then to pour in water and shake up, and then to wash with water until the rinsings are no longer acid.* Before being charged with water, the bottle should be rinsed out with some of the same kind of water as that which is to be analysed. The bottle having been charged with the sample of water, care must be taken

* In cases where a complete mineral analysis is required, and where alkalinity and sulphates are to be determined, it is safest to omit the washing with *acid*.

that it should be nearly but not quite full; and that having been attended to, the stopper should be inserted and tied over with a piece of clean linen or calico.

The employment of linseed meal, almond paste, &c., as lutings, is to be most strenuously avoided; but if anything of the sort be required, a little sealing-wax is perhaps the least objectionable.

Although it is preferable to have a glass stopper, still a clean new cork will do, and in the course of our experience we have never known any harm to arise from a clean cork. The sample of water should be kept in a cool and dark place until it is examined; and the examination should, if possible, take place within forty-eight hours after the collection of the sample.

In making examinations of the water-supply to towns, it is well to draw the water direct from the street mains; and the water-jets at the cab-stands in London offer special facilities for the collection of samples of the water supplied by the different Water Companies. In order to get a fair sample, it is a wise precaution to allow a little water to run away, so as to clear the pipe before collecting the sample.

If the water to be examined be that of a river or pond, the entrance of scum into the bottle should be avoided by immersing the bottle in the water, and taking care that the mouth shall open at a little distance below the surface. In the case of the river, the middle of the stream should be selected, and the outlets of sewers and feeders should be avoided; a note should also be made whether there has been heavy rain or long drought.

CHAPTER II.

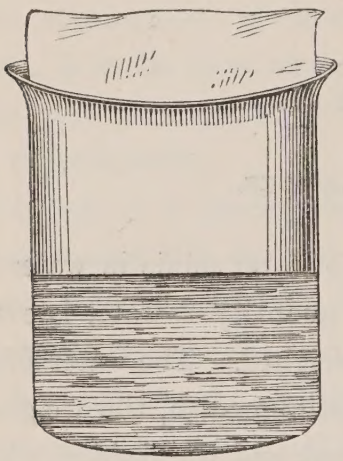
TOTAL SOLID RESIDUE.

THE determination of the amount of total solids in water is a very simple operation. A known quantity of water is evaporated to dryness, and the residue weighed. The water should be evaporated to dryness in a platinum dish, the weight of which has been previously ascertained, and the residue, which, after the water has evaporated away, adheres to the dish, is subsequently weighed along with the dish.

The exact details of the operation are the following:—The platinum dish is cleaned so as to be quite bright. It is then put into hot water, wiped, and allowed to remain for a few minutes in contact with a massive piece of iron (a flat smoothing-iron, with the handle knocked off, will answer very well), or else it may be left to cool in contact with a slab of porcelain.

Having been thus got into exactly the same condition as it will be in after the evaporation, it is to be weighed. Then it is to be placed in the water-bath, which consists of a beaker containing boiling water, and of such a size that the platinum dish may rest conveniently in its mouth (*vide* fig.). A small piece of filter paper may be inserted between the dish and the glass, in order to allow vent for the steam. Into the platinum dish 70 cubic centimeters of the sample of water are to be poured, the water in the bath is then set to boil by

help of a lamp, and kept boiling until the water in the platinum dish has evaporated away. In the course of an hour this will have taken place, and the residue in the platinum dish will soon dry. The dish is allowed to remain in the bath for about ten minutes after it appears to be dry (in order to ensure complete dryness), and then removed from the bath, wiped externally, allowed to cool for a few minutes in contact with the iron or porcelain, and weighed. If the weight of the empty dish be subtracted, the weight of the water-residue will be obtained.



In this way we obtain the weight of the solid residue left by 70 c. c. of water. Now, one gallon of water weighs 70,000 grains, and 70 c. c. of water weighs 70,000 milligrammes; so that 70 c. c. of water is a sort of miniature gallon, wherein the milligramme corresponds to the grain. If we know the number of milligrammes of residue which 70 c. c. of water leave, we know the number of grains of solids in a gallon of the water. To make everything clear we give an example:—

Quantity of the sample of water taken, equals 70 c. c.

Weight of dish and residue .	55·500 grammes.
Weight of empty dish . .	55·421 „
	·079

Therefore the total solids in this sample of water amounted to 79 grains per gallon.

In taking the total solids in water, a number of little modifications of the process, as above described, may be made. Instead of being contented with a simple drying at 100° C. in the water-bath, some chemists prefer a drying at 130° C. in the air-bath. Instead of taking only 70 c. c. of water, a larger quantity may be taken; and this is advisable if the balance or weights at the disposal of the operator be defective.

Very concordant results, and results quite good enough for all practical purposes, may, however, be obtained by operating on small quantities of water. Thus we have obtained

71·89 grains of solids per gallon,
72·10 „ „ „

in two experiments on the same sample of water; and also

24·64 grains of solids per gallon,
25·13 „ „ „

It will sometimes happen that the solid residue is very deliquescent; in such a case it must be rapidly weighed.

The evaporation of large quantities of water involves error, from dust getting into the water, and a certain amount of destruction of the organic matter present in the water, and the advantages gained by having a larger water-residue to weigh are counterbalanced by the error arising from the prolongation of the evaporation.

In order to give an idea of the amount of solid residue which actually occurs in natural water, we subjoin a few examples—

	Grains of total solids in a gallon.
London. Thames Companies . .	18·5
„ New River	17·6
„ Kent Company . . .	26·5
Manchester Water Supply . . .	4·7
Glasgow. Loch Katrine . . .	2·3
Bala Lake	3·2
Guildford. New Supply . . .	19·7
Scarborough Reservoir	28·7
The Rhine at Basel	11·8
Spree at Berlin	8·0
Atlantic Ocean	2688·0
Distilled water	0·1

With the exception of the sea-water, all these waters are, so far as the total solids are concerned, fit to drink; and, on inspecting the above table, it will be seen that the water supplied to the Metropolis contains four or five times as much solid matter as the water supplied to Manchester and to Glasgow. The healthiness of London is higher than that of Manchester and Glasgow; and although we should be unreasonable if, overlooking the fact that sanitary conditions are very numerous and very complex, we were to attribute the superior healthiness of the Metropolis to the state of its water-supply exclusively, we are, I think, warranted in maintaining that a high solid residue in drinking-water can have no very markedly injurious effect on the public health; and that the experience of London proves it.

In the instance of the London water-supply, the major part of the solid residue consists of carbonate of lime; and if we subtract the carbonate of lime, the rest of the solid residue will be seen to be not very much higher than that of the water of Manchester and other naturally soft waters.

The excellent new water-supply to Guildford is likewise in

the same predicament. According to an analysis made a few years ago, this water contains 14·7 grains of carbonate of lime, and 5 grains of other salts, including sulphate of lime. Of the nature of the solid residue in the Scarborough water, we have not at hand any very specific information; but most probably the same will be found to hold good in that case.

In the course of his work, after the water-analyst has obtained the solid residue and weighed it, he will do well in making a slight examination of it. If a few drops of hydrochloric acid be poured on it, effervescence will generally occur. This shows the presence of carbonates, which almost invariably consist of carbonate of lime. This qualitative examination for carbonates consumes hardly any time, and should hardly ever be omitted, inasmuch as a knowledge whether or not there are carbonates in the water is useful in various ways.

The water-residue in the platinum dish may likewise be gently ignited, and the observation recorded, whether it blackens during the ignition. The weight of the residue after ignition may likewise be taken. Formerly, before the recent development of water-analysis, the loss on ignition was regarded as a very important datum, and as indicating the quantity of organic matter in the water; but now we know that the loss on ignition is valueless for any such purpose. The only purpose which a weighing of the ignited residue now serves, is that it affords a check to the determination of total solids. In Part II., easy methods of determining the carbonate of lime in water will be described. One of these methods depends upon a measurement of the alkalinity coupled with the degree of hardness. The other requires a

determination of insoluble residue. We do not include them in this chapter, because they are not usually required in the ordinary analysis of potable water.

In conclusion, we will remark that if the solid residue do not exceed 30 or 40 grains per gallon, the amount of solids affords no reason for rejecting the water for domestic use.

CHAPTER III.

CHLORINE.

CHLORINE occurs in drinking-water usually in combination with sodium. Occasionally it occurs in combination with calcium or magnesium. Provided it be not very excessive, the amount of chlorine in drinking-water is, in itself, a matter of very little importance; for since common salt is an article which we require and take, in some shape or other, every day of our lives, it can be of very little consequence whether or not we take some of it in the water which we drink. The water-analyst resorts to measurements of the chlorine in water, because the presence of chlorine is, in some indirect manner, an indication of sewage contamination.

In order to understand how this comes about, and also to what extent chlorine is indicative of sewage, a little explanation will be necessary. In the first place, natural water which is uncontaminated with sewage is often almost free from chlorine. Urine and sewage, on the other hand, are, comparatively speaking, highly charged with chlorine, which usually exists in them in the form of common salt.

If then a given sample of water be found to be devoid of chlorine, or very nearly devoid of chlorine, it cannot have been charged with sewage. Hence, it occasionally happens that the finding of little or no chlorine in water is a valuable

criterion of purity. Here, however, the remark may be made that animal or sewage contamination is not the only organic contamination. Vegetable contamination is undoubtedly to be avoided in drinking-water, and against this form of contamination the absence of chlorine is no guarantee. When water is found to contain much chlorine, there is reason for suspecting the presence of sewage; and a further examination of the water is called for.

I am of opinion that too much stress has been laid on the chlorine in drinking-water, inasmuch as it is by no means rare to find an excessive quantity of chlorine in very pure water; and I know that, by reason of the chlorine, pure water has been condemned by water-analysts.

The circumstances in which chlorine-determinations in drinking-water would be of most service, are when time presses, and when, the general character of the water of the district being known, it is required to pronounce at once on the condition of a number of wells. Such a case might arise during an outbreak of cholera, when it might be necessary to decide at once on the character of all the wells of a town; and such is the ease with which the chlorine may be measured, that a hundred waters might be examined by one man in the course of a day. At such times I can conceive that the determination of the chlorine in drinking-water might prove of inestimable value.

In order to make a determination of chlorine in drinking-water, we avail ourselves of the well-known reaction of silver-salts on soluble chlorides. When a solution of nitrate of silver is mixed with a solution containing chlorides, the insoluble chloride of silver is produced; and the quantity of chlorine in water may be determined by ascertaining how

much of a standard solution of nitrate of silver is required, in order to precipitate all the chlorine in a certain volume of the sample of water.

The standard solution of nitrate of silver is made by dissolving 4·79 grammes of pure nitrate of silver in one litre of distilled water. This solution is then of such a strength, that one cubic centimeter of it is capable of precipitating exactly one milligramme of chlorine.

If some of this standard solution be dropped into a water containing chlorine, a white precipitate of chloride of silver will continue to form, until all the chlorine in the water has been used up; but, as may be readily seen on making the experiment, there is some difficulty in observing the exact point at which the formation of the precipitate ceases. This difficulty is overcome by using an indicator, which consists of a little chromate of potash. If this be employed, the exact point at which the formation of chloride of silver stops will be marked by the appearance of the deep-red chromate of silver.

The principle upon which the indicator depends is, that silver combines with chlorine in preference to chromic acid, and that, accordingly, no red chromate of silver is capable of being formed so long as chlorides are in the water, but that red chromate of silver instantly forms the moment the nitrate of silver is in the slightest excess.

The details of the analysis are as follows:—

70 c. c. of the sample of water is placed in a clean and white porcelain dish. A small quantity of yellow chromate of potash (about 30 milligrammes) is next placed in the water, and stirred up with a glass stirrer until it colours the water distinctly yellow. That having been done, the standard

solution of nitrate of silver, which should be contained by a properly graduated pipette, is carefully dropped into the water, which is stirred during this operation. The addition of the silver-solution is continued until the red colour, which forms as the silver-solution touches the water, becomes permanent on stirring. The very earliest point at which the chromate of silver becomes persistent should be read.

Certain precautions ought to be taken in performing these operations. The necessity of the chromate of potash being free from chlorides is almost too obvious to require mention. Suffice it to add, that there is now no difficulty in meeting with this substance in a state of sufficient purity in commerce. Neither the nitrate of silver nor the sample of water should be acid. If, as occasionally happens, the water be acid, it may be neutralised with pure carbonate of soda; or, indeed, it may be rendered faintly alkaline with advantage.

The reason why acidity has to be avoided is, that chromate of silver is dissolved by acids; and in the determination of chlorine it is my practice, after having noted down the exact point at which the liquid becomes red, to run in about one cubic centimeter of the silver-solution in order to make sure that there is no free acid. A very proper precaution to take is to make a blank trial with distilled water, and also a trial with water containing a known quantity of chlorine, before beginning the analysis. As has been above directed, the quantity of water to be taken for the determination of chlorine is 70 c. c. This is the miniature gallon in which the milligramme is the representation of the grain. If, then, we know the number of cubic centimeters of silver-solution which is required in order to use up all the chlorine, we know the number of milligrammes of chlorine in the 70 c. c. of water;

and consequently we know the number of grains of chlorine in a gallon of the water.

As will be found on actually trying this process, this determination of chlorine is made with great facility and rapidity. For most purposes sufficient accuracy is secured if the operation be performed on the small scale above described, and, as will be found, the error of experiment may be easily limited to 0·1 cub. cent., even when so little as 70 c. c. of water is operated upon. If a higher degree of accuracy be desired, it may be attained by taking double or treble that quantity of water, and evaporating it down to a small bulk before proceeding with the titration.

By way of example, we give the following table of the chlorine in a number of samples of water :—

	Grains of chlorine per gallon.
Bala Lake (*Wales*)	0·7
Ullswater (*Cumberland*)	0·7
The Rhine at Bonn	0·6
Thames Companies in London . .	1·2
New River Company, London . .	1·1
The Kent Company, London . . .	1·75
Guildford, New Water Supply (*Surrey*) .	0·9
Leek (*Staffordshire*), Town Water . .	0·7
Leek (*Staffordshire*), Workhouse Well .	0·5
Tunbridge Wells	3·7
London—Pump in Portland Place . .	2·2
„ Pump in Goodge Street . .	12·4
„ Pump in Oxford Market . .	33·2
Well in Windsor	6·9
Sample of Sewage	9·9

CHAPTER IV.

ORGANIC MATTER—FREE AND "ALBUMINOID" AMMONIA.

THE determinations of solids and of chlorine, described in the preceding chapters, are only of secondary importance in comparison with determinations of organic matter in drinking-water; and it is to the latter that the water-analyst should chiefly direct his attention.

The earliest method of estimating the organic matter was by the loss on ignition. The solid residue got on evaporating a given volume of water to dryness was carefully dried, weighed, ignited, and again weighed; and the difference in weight before and after ignition was taken to represent organic matter. To this procedure there are very many objections. The loss on ignition, besides including the amount of organic matter dissipated or burnt during the ignition, included much else. There was loss of carbonic acid from the carbonate of lime, and loss of water when a hydrated salt, such as sulphate of lime, became an anhydrous salt, and there was loss of acid from magnesian salts if they happened to be present in the solid residue. An attempt was made to get over these difficulties by the employment of a small and known weight of carbonate of soda, which was put into the water before evaporation to dryness, and the weight of which was afterwards subtracted from the weight of the water-residue. The loss of carbonic acid from the carbonate of lime was

repaired, by careful treatment, with solution of carbonic acid and redrying at 130° C. By these devices, as those can testify who have worked the process, it was quite possible to get very constant results; but having got the results, new difficulties started up, and it was shown that there still remained the loss in weight, occasioned by the destruction and dissipation of the nitric acid which exists in considerable quantities in most drinking-waters. When a water-residue is ignited, it loses nitric acid, and gains the equivalent of carbonic acid; and the loss in weight involved by this exchange is far larger than the organic matter. In consequence of the adoption of the ignition-process for the estimation of the amount of organic matter in water, a very exaggerated estimate of quantity of organic matter actually present in waters used to prevail among chemists. Thus the organic matter, as determined by this process in the water supplied by the Thames Companies to London, was from 15· to 17· parts per million (or a little over one grain per gallon). The water of the Kent Company, which is now known to be all but absolutely devoid of organic matter, showed, in like manner, a loss on ignition amounting to 16·5 parts per million. In truth, however, these numbers do not so much represent organic matter, as exchange of nitric acid for its equivalent of carbonic acid; and chemists have been agreed for some years in rejecting the ignition-process in the estimation of the organic matter in drinking-water.

The next process which was tried was the permanganate-process. A dilute solution of permanganate of potash, of ascertained strength, was prepared. To a given volume of the water to be tested, this standard solution of permanganate was added as long as it was decolorised by the water. From

the quantity of permanganate destroyed, the quantity of oxygen taken up by the water could be calculated, and waters could be compared together as to their deoxidising powers. This process was a great advance on the ignition-process, but still it did not prove to be satisfactory, and has been to a great extent abandoned. One of its striking advantages over the combustion-process was that the preliminary evaporation to complete dryness (which risks loss and destruction of organic matter) was altogether avoided. The defects of the permanganate-process are its want of delicacy, and also the circumstance that albumen is not readily attacked by the standard solution of the permanganate.

The next process which we shall mention is very unsatisfactory in every way. Instead of estimating the organic matter by loss on ignition, an attempt was made to perform an organic analysis of the dry water-residue, and to determine the carbonic acid and nitrogen resulting from its combustion with excess of oxide of copper and chromate of lead. This method was proposed by Dr. Frankland, and brought out by Drs. Frankland and Armstrong in the year 1868, and an account of it may be found in the Journal of the Chemical Society for that year. To a great extent it was a going back to the errors of the earliest method. There was the risk of destroying the organic matter during the evaporation to dryness in the water-bath. The nitric acid, which was one of the great sources of difficulty in the ignition-process, remained a source of difficulty in Frankland and Armstrong's process. As may be seen, on referring to the account of the process in the Journal of the Chemical Society, Frankland and Armstrong sought to destroy the nitrates by means of sulphurous acid applied to the water during its evaporation

to dryness. It is true that the nitric acid may be utterly destroyed in that manner, but it is only too plain that that cannot be done without destruction of the organic matter; so that the analyst who should attempt to work the Frankland and Armstrong process is placed in the dilemma of either leaving nitrates in the water-residue, or else of destroying the organic matter before making the combustion.

The circumstance that the amount of nitric acid far exceeds the organic matter, imparts special importance to this difficulty.

Another fatal difficulty of the process depended upon the minuteness of the organic matter in drinking - water. The quantity of organic matter in a litre of water (and that is the quantity which Frankland and Armstrong evaporated to dryness to yield the water-residue for one analysis) is too little to admit of an organic analysis. Frankland and Armstrong have published some determinations of organic matter in a litre of water, and exhibit a greater experimental error than the total quantities which occur in water of average goodness.

In short, the process is thoroughly untrustworthy, and being also very difficult and costly, has not met with general acceptance.

The methods of determining the organic matter which we have just described are methods of the past, and have only an historical interest. We next pass on to the method which is now in general use among chemists, and which is known as the ammonia-process, giving, as characteristic data, the "Free ammonia" and "Albuminoid ammonia" yielded by waters.

This method dates back to the year 1867, when it was

brought out by Smith and ourselves in a paper read before the Chemical Society on the 20th of June in that year. In its earliest form it was described in that paper, which was published later, in the year 1867, in the Journal of the Chemical Society. As originally described, there were two distinct modifications of the process, and at the time of the publication of that paper the precise distinctions between the two modifications were little understood. Later in the year 1867 a second paper bearing on the subject was read; and in the spring of 1868, further researches bearing on the subject were published by us in the Journal of the Chemical Society, and the first edition of this treatise was published. Except the ammonia-process, there never was a new method of analysis which, within a week or two of its discovery, at once assumed its definite form—a form to which many thousands of analyses brought no essential modification. On the 20th of June 1867, two varieties of the water-process were described, and preference was given to one of them; and to-day, after many thousands of these analyses have been made by many chemists in all parts of the world, the method of operation is still the process to which preference was given in 1867; and the method which we are about to describe differs in *no essential* particular from that described in 1867.

The ammonia-process, like the permanganate-process above described—and as every adequate method for the determination of its organic matter in water must do—operates on the water itself, and not on the residue got on evaporation. The principle of the method is measurement of the nitrogenous organic matter in waters by the quantities of ammonia yielded by the destruction of the organic matter. For the measurement of the quantities of ammonia, the very delicate Nessler

test is utilised. The agents used for the destruction of the organic matter are permanganate of potash and enormous excess of caustic potash; and, moreover, the destruction is effected at the boiling point of the solution.

A very laborious investigation, carried out by ourselves in the year 1868 (*vide* * Journal of the Chemical Society, May 1868), showed the wide applicability of the process, and justifies the conclusion that the ammonia-process, under the form in which we use it, is adequate to the measurement of the nitrogenous organic substances which occur in drinking-water. In the ammonia-process we have in fact a sort of combustion process with ammonia for the ultimate product, the peculiarity of the combustion being that it takes place in presence of the half or a quarter of a litre of water.

The details of the ammonia-process will now be given.

The following chemicals and apparatus are required for the performances of the analyses:—

1. The Nessler Reagent.
2. Dilute standard solution of Ammonia.
3. Solution of Potash and Permanganate of Potash.
4. Carbonate of Soda.
5. Distilled Water.
6. Retort.
7. Liebig's Condenser.
8. Lamp and Retort-Holder.
9. Glass Cylinders for Nessler test, or Nessler glasses.
10. Half-litre flask.
11. Measure for Solution of Potash and Permanganate of Potash.
12. Graduated Burette.
13. Pipette for Nessler Reagent.
14. Bottles, &c.

(1) *The Nessler Reagent* consists of a solution of iodide of

* *Vide* Appendix.

potassium saturated with periodide of mercury, and rendered powerfully alkaline with potash or soda. It is prepared by taking 35 grammes of iodide of potassium and 13 grammes of corrosive sublimate, and about 800 c. c. of water. The materials are then heated to boiling, and stirred up until the salts dissolve. That having been accomplished, a cold saturated solution of corrosive sublimate in water is cautiously added until the red periodide of mercury, which is produced as each drop of the solution falls into the liquid, just begins to be permanent. In this manner we obtain the solution of iodide of potassium saturated with periodide of mercury, and it remains to render it sufficiently alkaline, and to render it sensitive. This is accomplished by adding 160 grammes of solid caustic potash, or 120 grammes of caustic soda, to the liquid, which is afterwards to be diluted with water, so that the whole volume of the solution may equal one litre. In order to render the Nessler reagent sensitive, it is mixed finally with a little more cold saturated solution of corrosive sublimate, and allowed to settle.

When properly prepared, the Nessler reagent has a slightly yellowish tint. If it be perfectly white, it is sure not to be sensitive; and requires a further addition of solution of corrosive sublimate in order to render it sensitive. Before being employed, it should be tested to ascertain its condition. For this purpose about 2 c. c. of the Nessler reagent are dropped into a very weak solution of ammonia (strength about 0.05 milligramme of NH_3 in 50 c. c. of water), and if it be in proper condition, it will *at once* strike a yellowish-brown tint with the solution.

The stock of Nessler reagent should be kept in a well-stoppered bottle, from which a little is poured out from time

to time into a smaller bottle used to contain the Nessler reagent, which is about to be used.

(2) *Dilute standard solution of Ammonia.*—It will be found convenient to keep two solutions, a stronger solution and a weaker solution. The stronger solution is made by dissolving 3.15 grammes of chloride of ammonium in one litre of distilled water. (The commercial sal ammoniac, in dry fibrous crystals, answers very well for the purpose.) If the solution be prepared, as has just been described, it will contain one milligramme of ammonia in one cubic centimeter of solution. The weaker solution is prepared by diluting the stronger one with 99 times its volume of distilled water. The weaker solution, which therefore contains $\frac{1}{100}$ milligramme of ammonia in one cubic centimeter, is generally useful.

(3) *The solution of Potash and Permanganate of Potash* is made by dissolving 200 grammes of solid potash and 8 grammes of crystallised permanganate of potash in a litre of water. The solution is boiled for some time, in order to get rid of all traces of ammonia and organic nitrogenous matter; and after about one quarter of the liquid has boiled off, it may be filled up with pure distilled water, so as to bring the solution up to the litre. Each water-analysis requires 50 c. c. of the solution; wherefore each analysis consumes 10 grammes of potash and 0.4 grammes of permanganate.

(4) *Carbonate of Soda.*—A saturated solution of carbonate of soda may be prepared by boiling an excess of the common carbonate with water; and about 10 c. c. of the solid saturated aqueous solution is the proper quantity to use in a water-analysis. Instead of solution, the recently ignited solid carbonate may be employed. The object of the carbonate of soda is to expel the free ammonia from water which is acid It is, however, as a rule, not necessary to employ it.

(5) *Distilled Water.*—This is required for the making up of the various standards of ammonia, as will presently be explained. It must be very free from ammonia; so nearly free that in 100 c. c. of it there is not .005 milligramme of ammonia. Such water is not to be bought, but has to be prepared by the water-analyst expressly for the purpose. A good river or spring water is distilled in a clean retort or still, and the first portions of distillate are rejected. By and by water will distil over in a state of sufficient purity. The distillation must not be pushed too far, otherwise the latter portions of the distilled water may contain ammonia. In my own laboratory I make the same retort and condenser serve for the preparation of distilled water, and for the performance of water-analysis.

(6) *Retort.*—The size of retort which is suitable for water-analysis holds rather more than a litre when it is quite full. The retorts should be tubulated, and may be either corked or stoppered; the latter, however, seems preferable.

(7) *The Liebig's Condenser.*—A large condenser will be found to be suitable. In my own laboratory I use a large copper condenser, 60 centimeters long, and 7 centimeters in diameter; the glass tube which passes through it having a diameter of about 3 centimeters, and a length of about 90 centimeters. As will be perceived, the glass tube of the condenser is wide enough to admit of the beak of the retort entering it, without being drawn out by the blow-pipe. The most convenient packing is a little writing-paper, which is wrapped round the neck of the retort where it enters the tube of the condenser.

(8) *Lamp and Retort-Holder.*—A large Bunsen burner affords a convenient source of heat during the distillation. As will be explained, we apply the naked flame to the retort. The

retort-holder should be very steady and massive. We are in the habit of using a very well-known description of clamp made of metal, and lined with cork where it clips the neck of the retort. The incline of the retort-holder must be carefully adjusted to the incline of the condenser, so that the retort may be retained in position without any unnecessary pressure. The employment of a ring to support the retort from below is not to be recommended. Much of the ease of the working of the process depends upon the proper mounting of the retort, which ought to admit of the easy removal of the retort, and easy remounting of it.

(9) *Glass Cylinders for Nessler test, or Nessler glasses.*— These should be of perfectly white glass. In my own laboratory the Nessler glasses are cylinders, 17 centimeters in height and 4 centimeters in diameter. They are marked with a file-mark at 50 c. c. capacity. From half a dozen to a dozen are necessary. I use also a white porcelain tile for them to stand upon when they are used.

(10) *A half-litre flask* to measure out the sample of water is required. It should never be used for organic fluids, and indeed it is best to keep it exclusively for water.

(11) *The measure for solution of Potash and Permanganate of Potash* is a convenient glass, with a simple mark at 50 c. c. capacity. To pour well is an essential qualification that such a glass should possess. I am in the habit of using a thick glass-vessel, which is an apothecary's dispensing four-ounce measure, and which I bought in an ungraduated state.

(12) *A Graduated Burette*, divided accurately into cubic centimeters, and provided with a glass stopcock, is used for measuring out the dilute standard ammonia. It is held by any convenient holder.

(13) *The Pipette for Nessler Reagent* is made of a piece of glass tube, and requires just one file-mark at the 2 c. c. capacity.

(14) *Bottles* are required to hold the different solutions. It is of importance that the bottle holding the solution of potash and permanganate of potash should pour well. A large glass funnel is also required.

The convenience of having a water-supply and sink close at hand will be readily appreciated. It will also be found to be advantageous to keep a table, or part of a table, appropriated exclusively to water-analysis, and to appropriate a set of apparatus to it. Thus the funnel, the half-litre flask, the retort and condenser, burette, pipette, and Nessler glasses, should not be used for anything else but water-analysis.

One very important matter in testing of this order of delicacy is the cleaning and washing out of the apparatus; and it should be borne in mind that all glass surfaces which have been exposed to the air for any length of time are liable to contract traces of ammonia from the air; and the rule which has to be observed, in order to ensure accuracy, is to wash out with clean water immediately before use. Furthermore, it may be remarked that for these washings it is unnecessary to employ distilled water; and that the ordinary town water is, as a rule, everything that can be desired for the purpose. There should, however, be no stint of the quantity of water. The analysis is performed in the following manner:—

The retort having been washed out with a little strong acid (either hydrochloric or sulphuric acid), is then washed out with good tap water, until the few drops which drain out do not taste acid. It is then mounted in its holder, and

properly connected with the Liebig's condenser, either by means of a wide india-rubber tube, or else it is just packed into the condenser by means of a little writing-paper. Half a litre of the sample of water is next measured in the half-litre flask, and poured into the retort through a large funnel kept specially for the purpose. Then the stopper or cork, which must be kept scrupulously clean, is put into its place in the retort, and the Bunsen lamp is lighted, and the flame applied externally to the naked retort. The retort must be thrust right down into the flame, which, however, must not play upon the surface of the retort higher than the level of the liquid within the retort. In a few minutes the contents of the retort will begin to boil, and the water will begin to distil over. The distillate is to be collected in the glass cylinders for the Nessler test.

When 50 c. c. of distillate have distilled over, the cylinder is to be changed. The first 50 c. c. should then be *Nesslerised*, which will be explained further on. The distillation is to be continued until 150 c. c. have come over, and the 150 c. c. of distillate are to be thrown away. Having done so, and thereby reduced the contents of the retort from 500 c. c. (the quantity originally taken) to 300 c. c., the distillation is stopped for a moment.

Fifty cubic centimeters of the solution of potash and permanganate of potash, which has been described, is then to be poured into the retort through a wide funnel, and the distillation proceeded with.

At this stage of the operation it is sometimes necessary to shake the retort gently, in order to avoid bumping. This is especially the case in the analysis of very bad water. With a little practice, and a little presence of mind, the operator will

very easily overcome difficulties of this description. The distillation must be continued until 50 c. c. of distillate have come over, and this must be collected in a cylinder for Nesslerising. A second 50 c. c. must be collected in another Nessler cylinder, and a third 50 c. c. must be collected; and that having been done the distillation may be stopped, and the apparatus left standing until it is required for another analysis.

Nesslerising, which has been mentioned in the above passage, is the operation of finding the strength of dilute solutions of ammonia by help of the Nessler test—a test discovered by a chemist named Nessler. The preparation of the Nessler reagent has already been described in detail. Let it be required to tell how much ammonia is present in 50 c. c. of distillate contained in one of the cylinders above mentioned.

For this purpose 2 c. c. of Nessler reagent are dropped into the 50 c. c. of distillate. This is best done by aid of the appropriate 2 c. c. pipette above mentioned. The pipette also serves as a convenient stirrer, to stir up the liquid after the addition of the Nessler reagent to it. If the 50 c. c. of distillate contain any ammonia, it will soon after the addition of the Nessler reagent, as just described, assume a rich brown colour; and the more the ammonia, the deeper the colour.

The next step is to imitate the depth of colour given by the distillate. In order to do so, a clean cylinder is taken, and into it is dropped a certain measured volume of the standard solution of weak ammonia, which is filled up with distilled water to the 50 c. c. mark on the cylinder. Two cub. cent. of Nessler reagent is then dropped into it by means of the pipette, and the whole is very thoroughly stirred up.

The 50 c. c. of distillate in its appropriate cylinder, and the 50 c. c. of water containing the standard ammonia, are then placed side by side on a white surface (a white porcelain tile answers very well), and carefully looked through, and a judgment is arrived at as to which is of the deeper colour. If they be of equal depth, the Nesslerising is accomplished, inasmuch as the quantity of ammonia required to imitate the colour, which Nessler reagent imparts to the distillate, is the quantity of ammonia in the distillate. If the two solutions be not of equal depth, another standard must be made up with water, dilute standard ammonia, and Nessler reagent, and another comparison must be made.

With a little practice Nesslerising becomes very easy.

In the course of a water-analysis it will be perceived that ammonia is to be looked for at two stages: firstly, before the addition of the potash and permanganate; and secondly, after the addition of the potash and permanganate. The ammonia which comes over in the first stage is the "free ammonia," and that which comes over in the second stage is the "albuminoid ammonia."

The recommendation has been given to Nesslerise only the first 50 c. c. of free ammonia, and to throw away the next 150 c. c. Formerly it was our custom to Nesslerise all four 50 c. c. of free ammonia; but that was a useless trouble, inasmuch as the first 50 c. c. invariably contains three-quarters of the total amount of free ammonia. The rule is, therefore, to Nesslerise the first 50 c. c. of free ammonia, and then to add one-third. Thus, if in the first 50 c. c. of distillate the quantity of ammonia were found to be 0.02 milligramme, the total free ammonia would be 0.027 milligramme.

In the instance of the albuminoid ammonia, it is necessary to Nesslerise each separate 50 c. c. of distillate, and to add

the amounts together, in order to arrive at the total albuminoid ammonia.

Since half a litre of water is taken for the analysis, the results must be multiplied by two, in order to make them count upon the litre; and if that be done, we shall then have the "free ammonia" and "albuminoid ammonia" expressed in milligrammes per litre, or in parts per million (which is the same thing).

The following example of the manner in which the notes of a water-analysis are kept in the laboratory may be useful.

Half a litre of water was taken for analysis.

Free ammonia . .	.01	milligrammes
(Correction) . .	.003	,,
	.013	
Albuminoid ammonia .	.035	,,
,, . .	.015	,,
,, . .	.000	,,
	.05	

Therefore, in litre—Free ammonia . = .026
Albuminoid ammonia = .10

The following analysis done by ourselves on various occasions may be cited in illustration of the results to be looked for. We have found the water of the river Thames, as supplied by the various companies, as follows:—

Date.		(Parts per million milligrammes per litre.) Ammonia. Free.	Albuminoid.
1867.			
July	West Middlesex Water Co. .	.01	.07
,,	,, ,, .	.01	.06
,,	,, ,, .	.01	.06
,,	,, ,, .	.01	.06
1868.			
July 29.	,, ,, .	.01	.09

Date.			(Parts per million milligrammes per litre.) Ammonia. Free.	Albuminoid.
1872.				
Oct. 3.	West Middlesex Water Co.	.	.01	.07
Dec. 3.	,, ,,	.	.00	.10
1873.				
Jan. 2.	,, ,,	.	.00	.08
1867.				
July	Grand Junction Company	.	.01	.08
,,	,, ,,	.	.01	.07
,,	,, ,,	.	.01	.07
,,	,, ,,	.	.01	.07
1872.				
Oct. 8.	,, ,,	.	.00	.07
Dec. 5.	,, ,,	.	.00	.16
1867.				
July	Chelsea Company	.	.01	.07
,,	,, ,,	.	.01	.10
1872.				
Oct. 5.	,, ,,	.	.00	.06
Dec. 2.	,, ,,	.	.02	.13
1867.				
July 6.	Southwark and Vauxhall	.	.03	.16
,, 18.	,, ,,	.	.02	.12
,,	,, ,,	.	.01	.15
1872.				
Feb. 7.	,, ,,	.	.01	.12
,,	,, ,,	.	.01	.09
,,	,, ,,	.	.01	.12
Oct. 2.	,, ,,	.	.06	.12
,, 12.	,, ,,	.	.06	.13
,,	,, ,,	.	.06	.12
Dec. 2.	,, ,,	.	.00	.18
1867.				
July 19.	Lambeth Water Company	.	.02	.14
,, 20.	,, ,,		.02	.15
1872.				
Feb. 7.	,, ,,	.	.01	.14
Oct. 9.	,, ,,	.	.01	.10
Dec. 2.	,, ,,	.	.01	.16

Three of the Thames companies—viz., the West Middlesex, the Grand Junction, and the Chelsea—supply pure water during the summer months. During the winter months, however, the water supplied by these companies is by no means so pure as in the summer time. Two companies—viz., the Southwark and Vauxhall and the Lambeth—do not supply very pure water even in summer. The explanation of these results appears to be that, whereas the arrangements of the three first-named companies for the filtration of the water taken from the river are good, the arrangements of the Southwark and Vauxhall and of the Lambeth companies are defective. During the winter months the filters of all the Thames companies seem to be, in some degree, overtaxed. To make the investigation of the Thames companies complete, we have analysed the water in the river at Hampton Court, where the supply is withdrawn from the river to feed the reservoirs of the different companies.

On July 9th, 1867, we analysed water taken from the river Thames above Hampton Court, and obtained the following results :—

	(Parts per million.) Ammonia.	
	Free.	Albuminoid.
Sample I.	0.04	0.28
Sample II.	0.01	0.23

Such, then, is the raw material with which the Thames companies have to work ; such is the condition of the water of the Thames before purification by the companies.

We have, likewise, made repeated analyses of the water with which the New River Company serves the inhabitants of London.

Our results are as follows :—

Date.		(Parts per million.) Ammonia. Free.	Albuminoid.
1867.			
June 21.	New River Company . .	.02	.08
July 12.	„ „ . .	.01	.05
„ 20.	„ „ . .	.02	.05
Aug. 21.	„ „ . .	.00	.06
1868.			
Jan. 25.	„ „ . .	.02	.09
Aug. 1.	„ „ . .	.00	.08
1872.			
Oct. 2.	„ „ . .	.02	.08
Nov. 21.	„ „ . .	.01	.06

The water of the River Lea, supplied by the East London Water Company, we found as follows:—

		(Parts per million.) Ammonia. Free.	Albuminoid.
1867.			
June 18.	East London Company .	.03	.09
1872.			
Oct. 10.	„ „ .	.01	.04
Dec. 4.	„ „ .	.01	.18

The water which the Kent Company supplies to London, and which is derived from deep springs, is exceedingly pure, as is shown by the following analyses:—

		(Parts per million.) Ammonia. Free.	Albuminoid.
1872.			
Feb. 7.	Kent Company . . .	.01	.02
Nov. 20.	„ „ . . .	.01	.02

Even during the winter months this water preserves its character.

Leaving the Metropolis, we have analysed the water supplied to a number of towns.

		(Parts per million.) Ammonia. Free.	Albuminoid.
1867.			
Aug. 19.	Manchester town water . .	.01	.06
„	„ „ . .	.01	.06
„	„ „ . .	.01	.07
Sept. 18.	Edinburgh town water . .	.00	.07
Oct. 3.	Glasgow (Loch Katrine) town water	.00	.08
1871.	Chester (Dee) town water .	.00	.07
1871.	Scarborough (Yorkshire) town water	.01	.06
1873.			
July	Oxton (Birkenhead) town water	.00	.02
Aug.	Chelmsford (Essex) town water	.08	.02
„	Leek (Staffordshire) town water	.00	.02
Dec.	Fylde water-works, Lytham, in Lancashire . . .	.00	.10
1872.			
Feb.	New Supply to Guildford, Surrey	.00	.01

The following analyses of deep spring water, supplied by wells, have also been made :—

		(Parts per million. Ammonia. Free.	Albuminoid.
June 1867.	Caterham water . .	.04	.00
„ 1867.	Cold Harbour, Dorking .	.01	.00
May 1873.	Well in Frome, Somersetshire	.00	.02
Nov. „	Well water, Kirby Lonsdale, Westmoreland . .	.01	.03
„ „	Well at Chatham . .	.03	.03
„ „	Well, Henley-on-Thames .	.02	.02

Five springs in the West of England.

July 1868.					
	No. 1, containing	26 gr. solids per gal.		.00	.01
„	No. 2, „	23 „	„	.01	.04
„	No. 3, „	20 „	„	.00	.01
„	No. 4, „	52 „	„	.00	.01
„	No. 5, „	20 „	„	.01	.03

Our investigations warrant the following general conclusions :—

Deep spring water (which is water that has undergone a very perfect natural filtration) is often so pure as not to yield 0.01 parts of albuminoid ammonia per million; and, unless mixed with surface water, does not yield so much as 0.05 parts of albuminoid ammonia per million.

The *filtered* water supplied by water companies, no matter whether derived from a lake, from clean mountain streams, or from defiled rivers, yields from 0.05 to 0.10 parts of albuminoid ammonia per million; and, indeed, if the filtration be efficient, approximates to 0.05.

In the case of the Fylde water-works at Lytham (the number for which is 0.10 per million), the remark may be made, that this water is not filtered by the company; and our general conclusion is that, when the number rises to 0.10, there is defective filtration.

When the filters are overtaxed, as happens in the rainy season and in the winter, water companies supply imperfectly filtered water, in which as much as from 0.10 to 0.20 parts of albuminoid ammonia is found in a million parts of the water; and it is matter of observation that diarrhœa is frequently prevalent in communities which drink such water.

We have next to consider the analytical characters of water which is not fit to drink. Certainly the unfiltered water of the Thames, whether taken from the river at Hampton Court or at London Bridge, is unfit to drink; and certainly surface-wells, which contain excreta in a slightly altered condition, and which occasionally contain the *materies morbi* of cholera, or typhoid fever, yield undrinkable water. And certainly well-water, which is loaded with vegetable matter, is not fit

to drink. Examples of all these various kinds of bad water are now given. We begin with examples of water supplied by water companies in an imperfectly filtered condition, and we end with veritable sewage.

		(Parts per million.) Ammonia.	
		Free.	Albuminoid.
Dec. 1872.	Southwark and Vauxhall Co.	.00	.18
„	Lambeth Company* . .	.01	.16
Nov. 1873.	Great Yarmouth Water Co. .	.00	.18
„	Thames, a little above Hampton Court, unfiltered . .	.04	.28
June 1867.	Thames at London Bridge, at 2 hours' flood . . .	1.76	.35
„	High tide	1.02	.59
„	„	1.02	.56
„	„	1.02	.50
„ 1873.	Well at Leek workhouse .	.02	.34
„ 1867.	Great St. Helen's Pump, London	3.75	.18
„	Pump in Bishopgate St., London	7.50	.25
„	Pump in Drapers' Hall, London	6.00	.31
„	Pump in Edinburgh . .	.21	.29
„ 1873.	Well in Windsor (containing 48.5 grs. of solids, and 5.6 grs. of chlorides per gallon)	1.20	.08
„	Well in Eton (containing 48.5 grs. of solids, and 5.6 grs. of chlorine per gallon) .	.00	.84
Feb. 1872.	Effluent from Sewage . .	16.20	.90

From these examples it will be seen that the albuminoid ammonia is excessive in waters which are undeniably contaminated, and in most of them it is very excessive.

The appearance of free ammonia in many of these polluted waters is likewise a striking phenomenon, and requires a few words of comment. When the free ammonia exceeds 0.08 parts per million, it almost invariably proceeds from the fermentation of urea into carbonate of ammonia, and is a sign

* The water of the Lambeth Company has been improved since 1872.

that the water in question consists of diluted urine in a very recent condition. In these instances the water will likewise be found to be loaded with chlorides.

Much albuminoid ammonia (which generally comes over slowly), little free ammonia, and almost entire absence of chlorides, is indicative of vegetable contamination, and is exemplified by the well at the Leek Workhouse. Such water is very injurious to health.*

The analytical characters, as brought out by the ammonia process, are very distinctive of good and bad waters, and are quite unmistakable. There is, indeed, hardly any branch of chemical analysis in which the operator is less exposed to the risk of failure.

As will be found on subjecting "effluent waters," and certain very bad well-waters, to analysis in the manner above described, the first 50 c. c. of distillate from the half-litre of water will be so highly ammoniacal as to yield, on Nesslerising, a colour too deep to be accurately read off, or even will yield a precipitate with the Nessler reagent. Under these circumstances, one of two obvious devices may be adopted. In order to read, by the Nessler-test, the ammoniacal strength of the 50 c. c. of distillate, which cannot be Nesslerised in its undiluted condition, we may obviously dilute it to ten times its bulk, and then (having carefully mixed up thoroughly)

* In the Leek Workhouse there has been for years past a general tendency to diarrhœa, which could not be accounted for until the water was examined, and shown to be loaded with vegetable matter. The water was almost free from chlorine, containing only 0.5 grain per gallon. A well on Biddulph Moor, a few miles from Leek, yielded 0.5 grain chlorine per gallon, and .03 "free" and .14 albuminoid ammonia per million. The persons who were in the habit of drinking this water suffered from diarrhœa.

submit 50 c. c. of the diluted liquid to Nesslerisation. And, in a general way, if it be desired tc Nesslerise a concentrated ammoniacal liquid, the object may be attained by first diluting to a known extent, and then Nesslerising, and making a perfectly obvious calculation.

Another method of dealing with sewages, "effluents," and bad well-waters, is by diminution of the quantity to be operated upon; instead of a half-litre we may take 100 c. c., or even less. For this purpose, half a litre of freshly-distilled water is placed in the retort, and distilled until 50 c. c. of distillate have come over (this must not contain more than .01 or .02 milligramme of NH_3), and then, everything remaining *in situ*, and the whole apparatus being thus in a condition of guaranteed freedom from ammonia, the 100 c. c. of bad water may be dropped directly into the retort, and the operation proceeded with in the usual manner. In these cases the addition of carbonate of soda will generally be called for, and this substance should be freshly ignited before being employed.

APPENDIX.

When the ammonia-process was first brought out, the quantity of water taken for analysis was one litre, but it was very soon found that half a litre was a sufficient quantity for most practical purposes, and that, all things considered, that was the most convenient quantity to be taken. The degree of accuracy with which the Nesslerisings were made was within half a hundred of a milligramme.

I have, however, found that, with suitable apparatus and precautions, an accurate analysis of 100 c. c. of water may be

made, the Nesslerising being, in this instance, done to within one thousand of a milligramme.

I have analysed the same water on the two scales,—viz., taking a half-litre and 100 c. c. for the analysis,—and got the same results.

The apparatus to be employed consists of a little retort and narrow Liebig's condenser (figured on page 130, being the same which is used in the analysis of urine). The above-described solution of potash and permanganate of potash (strength 200 grammes of solid potash and 8 grammes of crystals of permanganate of potash to a litre of water), which has been previously boiled, so as to be absolutely free from ammonia and nitrogenous organic matter, is employed.

The operation is managed as follows:—

Firstly, The retort and condenser are to be made scrupulously clean, and are to be guaranteed as being clean. This is done by mounting the apparatus, charging the retort with 100 c. c. of tolerable drinking-water, and with 10 c. c. of the permanganate solution, and distilling till the distillate comes over clean—*i.e.*, free from ammonia. That being accomplished (and such a preliminary is absolutely necessary), we may proceed.

The retort is disconnected, and the solution of permanganate having been turned out, it is washed with clean tap-water, drained, and then charged with 100 c. c. of the sample to be analysed. Having been mounted and properly connected with the Liebig's condenser, the distillation is to be commenced, and when 10 c. c. have distilled over, the 10 c. c. of distillate is to be Nesslerised in a glass presently to be described. That having been done, 30 c. c. more are to be distilled off, and either Nesslerised or thrown away.

At this stage the distillation is to be interrupted, and 10 c. c. of the solution of potash and permanganate of potash are to be poured into the retort, and the operation continued so long as 10 c. c. of distillate shows a sign of ammonia.

The Nesslerising in these delicate operations is managed in glasses of thin, white glass, cylindrical in form, 10 centimeters long, and 1.5 centimeters broad, and closed at one end, so as to stand upright on a white porcelain tile. The charge of Nessler reagent is to be about 0.5 c. c. (instead of 2 c. c. as when working on the usual scale). It will, of course, be understood that $\frac{1}{1000}$ milligramme of ammonia is contained in 0.1 c. c. of the dilute standard solution of ammonia, and that the standard ammonia solution will require to be measured to the 0.1 c. c. in a suitable burette or pipette. The operator will not fail to notice that he will have no difficulty in distinguishing between $\frac{1}{1000}$ and $\frac{2}{1000}$ milligramme of ammonia in these little glasses, and that the colouration is particularly visible in the meniscus of the liquid.

In conclusion, a very obvious application of this delicate process may be referred to. If one litre of a given water (and it should be a tolerably pure specimen of water) be operated upon, the distillates may subsequently be submitted to distillation in the little apparatus, and so measurements of ammonia to the thousandth of a milligramme may be effected. In this manner, a litre (or a million milligrammes) of water will yield ammonia which is measured to the $\frac{1}{1000}$ milligramme, and in this manner distinctions may be made between waters which differ very slightly indeed in purity. I do not think that we are at present called upon to accomplish this task; but we are now ready if the need should arise.

CHAPTER V.

THE MOIST COMBUSTION-PROCESS.*

As will be found on referring to the Discourse on the Analysis of Potable Waters, read to the Chemical Society in the year 1865 by the late W. A. Miller, the proposal to employ a solution of permanganate of potash for the measurement of the organic matter in drinking-water was first made by Forchhammer, of Copenhagen, so long ago as the year 1850; and, before the Ammonia-process came out, the permanganate-process had come into partial use among chemists. It has, however, always been pretty generally felt that the process was defective and unsatisfactory. This was strikingly illustrated by Dr. Frankland, who, in the year 1868, published the following results given by applying the permanganate to dilute solutions containing known quantities of organic matters :—

Name of substance (30 parts dissolved in 1,000,000 parts of water).	Oxygen absorbed during six hours.	Oxygen required for complete oxidation.
Gum arabic	0.35	35·5
Cane sugar	0.15	33·7
Starch	0.30	33·5

showing that not so much as one-hundredth of the oxygen required for total oxidation had been absorbed. I am inclined to regard these results as somewhat exaggerating the

* This process has been protected by letters-patent, and cannot be used without license.

defects of the process: but it admits of no doubt whatever that the permanganate-process, as hitherto worked, has been an abortive process, and that chemists have not hitherto used the permanganate-solution in an efficient manner.

I believe that distrust of the stability of the permanganate, and consequent fear of mistaking spontaneous alterations of strength for reduction brought about by organic matter, have prevented chemists from making an effective employment of this oxidising agent.

The moist combustion-process is the process of completely oxidising (or nearly completely oxidising) organic bodies by means of permanganates.

In the moist combustion-process, instead of cane sugar absorbing less than $\frac{1}{100}$ of its own weight of oxygen, an absorption of fully its own weight of oxygen is brought about.

The practical details of the moist combustion-process of Water Analysis are as follows:—

Four solutions are required.

(1) Solution of Permanganates: strength, one cubic centimeter containing one milligramme of active oxygen.

(2) Solution of Protosulphate of Iron: strength, one cubic centimeter absorbing one milligramme of active oxygen.

(3) Solution of Caustic Potash.

(4) Solution containing Sulphuric Acid.

I have ascertained that these solutions keep very well in stoppered bottles. In the course of four months I found that the iron-solution, which had been frequently used, in a bottle holding a litre, having been half-emptied, had only lost 0.5 c. c. per 10.0 c. c. in strength.

The apparatus requisite is a flask or retort, and an

arrangement for boiling, a litre-measure, a 5 c. c. pipette to discharge 5 c. c., and a 5 c. c. pipette graduated to 0.2 c. c.

The operation is performed thus :—

The retort employed for the ammonia-process may be used, and having been cleaned and mounted as if for the ammonia-process, is charged with one litre of the water to be examined. Before beginning to distil, 5 c. c. of the solution of caustic potash is dropped into the water contained by the retort, and then 5 c. c. of the solution of permanganate are very carefully measured, and likewise dropped into the retort, which is then heated and its contents rapidly distilled until about 900 c. c. have distilled over. That having been done, the heating is stopped, and the observation is made that the liquid remaining in the retort retains a pink colour. Then 10 c. c. of the solution of sulphuric acid are dropped into the retort and shaken up with the contents of the retort. Then 5 c. c. of the iron-solution are to be dropped into the retort, and in a few minutes the liquid will become quite colourless. That having been attained, the solution of permanganate of potash contained in the graduated pipette is carefully dropped into the liquid, and the point is accurately noted at which the red colour just begins to be permanent.

The following data will thereby be obtained :—

(*a*) Total number of c. c. of permanganate used up.

(*b*) Total number of c. c. of permanganate used up by the iron-solution.

The difference between these figures is the number of c. c. of permanganate consumed by the organic matter in one litre of water, or the number of milligrammes of active oxygen consumed by the organic matter in one litre of the water. An example will render this description intelligible.

One litre of the water supplied by the Southwark and Vauxhall Water Company was placed in the retort, and 5 c. c. of the potash-solution and 5 c. c. of the permanganate-solution were added. The distillation was then continued till only a small bulk of liquid (100 c. c.) remained in the retort; 10 c. c. of the sulphuric acid was then added, and 5 c. c. of iron-solution, which rendered the liquid quite colourless. Then the permanganate-solution was run in until a red colour just formed and did not vanish on shaking up: 3.7 c. c. being required for this purpose.

We have, therefore:—

	c. c.
Total permanganate used	8.7
Permanganate used by the 5 c. c. of iron-solution	5.0
Permanganate consumed by the organic matter in the litre of water. . .	3.7

Or, one litre of this sample of Southwark and Vauxhall water consumes 3.70 milligrammes of oxygen.

In analysing very bad waters it will be found that in the course of the distillation the 5 c. c. of permanganate-solution is exhausted. When this happens, another 5 c. c. of permanganate must be dropped into the retort, and the operation continued, care being taken to leave an excess of permanganate before the stage is reached at which sulphuric acid is added.

This is the place to call attention to a peculiarity of the action of permanganate-solution on iron-salts which has, I believe, occasioned the belief that there is a want of precision in the action. If the standard solution of permanganate be added to an acid solution containing proto-salt of iron, a point will soon be reached at which the faint pink colour ceases to

disappear on shaking up the solution, but after the lapse of a few minutes the pink colour gives place to a brownish precipitate. Probably this last destruction of permanganate is due to the formation of Ferric acid: but it takes place only after lapse of time, and the only consequence which results is that, in titrating iron-solutions with permanganate, the final reactings must be immediate, and not after lapse of time.

The moist combustion-process, as above described, will be found to involve no practical difficulties. It may be carried out either on a smaller or a larger scale, suitable modifications being made to meet the requirements of the case.

The following examples will serve to give some idea of the results obtainable on submitting different kinds of drinking-water to the process.

Waters of acknowledged purity have given the following numbers:—

	Oxygen consumed. Parts per million.
Carefully *redistilled* water	0.14
Distilled water	0.32
Filtered waters (through Silicated carbon filter)	0.48
Kent Water Company	0.48
Well in Croydon	0.40

Waters of average purity have given:—

			Oxygen consumed. Parts per million.
1878.	June 15.	New River Company . .	2.48
	May 17.	Chelsea Company . . .	2.28
1879.	Feb. 13.	Water from Isle of Wight .	1.90
	„ 12.	Uxbridge Artesian Well . .	2.40

The following are examples of polluted waters:—

	Parts per million.		
	Free Ammonia.	Albuminoid Ammonia.	Oxygen consumed.
Water from Isle of Wight	2.00	0.74	9.40
Water from Hillingdon	2.00	0.16	5.60
Water from Uppingham	0.02	0.14	4.00
Southwark and Vauxhall	0.04	0.12	3.70

The general conclusions to which the investigations point are—that water distinctly of first-class purity does not consume more than 0.50 milligrammes of oxygen per litre; that average drinking-water consumes between 2.00 and 3.00 milligrammes of oxygen per litre; and that dirty water considerably exceeds the latter figure.

In helping to decide between the difficult case of the ammoniacal deep-spring and sewage water the moist combustion is particularly useful.

CHAPTER VI.

POISONOUS METALS.

A HIGH degree of freedom from poisonous metals is demanded of drinking-water; and a special testing for lead, copper, and even iron, forms an essential part of the usual analysis of drinking-water.

The testing may be managed very simply and expeditiously, and also very delicately, by taking advantage of the formation of dark-coloured sulphurets by means of sulphuretted hydrogen, or sulphuret of ammonium. Moreover, these metals, in very dilute solutions, do not yield precipitates of sulphuret, but yield dark-coloured solutions, the depth of which is proportional to the amount of metal present. It is, therefore, possible to estimate these metals by the depth of the colour, and I believe the first attempt to do so was made by the late Dr. W. A. Miller.

The following are the details of the process, as performed in my laboratory :—

Standard solutions of lead, copper, and iron are prepared thus—

Standard solution of lead, containing one milligramme of lead in one cubic centimeter of solution, is made by dissolving 1.66 grammes of crystallised acetate of lead in one litre of water. Standard solution of copper, containing one milligramme of copper in one cubic centimeter of solution, is

made by dissolving 3.93 grammes of crystallised sulphate of copper in one litre of water.

Standard solution of iron, containing one milligramme of iron in one cubic centimeter of water, is made by dissolving 4.96 grammes of crystallised protosulphate of iron in one litre of water.

In order to find how much of these metals is contained in a water, the following process may be adopted:—

For iron: into 70 c. c. of the sample of water contained in a dish of white porcelain, a glass rod, which has been dipped in sulphuret of ammonium, is to be inserted, and the water is to be well stirred up. If iron be present, the liquid will assume a dark colour, and the amount of iron may be determined by imitating the colour by means of the standard solution of iron above described. The manner of operation will be obvious to all persons who are in the habit of measuring ammonia by the Nessler test.

Iron is not the only metal which gives a black precipitate with sulphuret of ammonium, and, as will be obvious, the getting of this black colour may be due to lead or copper, as well as to iron. The circumstance that the sulphuret of iron is dissolved by dilute acid serves to distinguish it from the sulphurets of lead and copper, which are not soluble in dilute acids; and in practice we first obtain the colouration in an alkaline solution, and then render slightly acid with a drop or two of hydrochloric acid, and observe whether or not the colour disappears or diminishes in depth. Disappearance of the colour, or even diminution of colour, on rendering acid, is a sign of the existence of iron in the liquid.

The manner of estimation of copper or lead is sufficiently obvious. The 70 c. c. of the sample of water contained in a

white porcelain dish is stirred round with a glass rod, moistened with sulphuret of ammonium, and is then rendered faintly acid with hydrochloric acid, and the depth of colour observed. That having been done, 70 c. c. of distilled water, into which a certain measured quantity of standard copper-solution, or standard lead-solution, has been put, is also treated with a drop of sulphuret of ammonium, and the resulting depth of colour compared with that given by the sample of water.

Good drinking-water ought not to contain more than $\frac{1}{10}$ or $\frac{2}{10}$ grains of iron per gallon; and should contain less than $\frac{1}{10}$ grain of lead or copper. It is unnecessary to make out whether the metal be lead or copper, for either would condemn the water.

As will be found out in practice, the $\frac{1}{10}$ grain of iron, lead, or copper in one gallon of water is quite visible, even if only the miniature gallon (*i.e.*, 70 c. c.) of the sample of water be operated on as above described. And, practically, the usual testing of potable water for metals resolves itself into the following very simple procedure. Seventy cubic centimeters of the water are placed in a porcelain dish, and stirred up with a glass rod, moistened with sulphuret of ammonium. The observation is then made whether or not there is any colouration. If there be colouration, it should only be just visible; and on adding two or three drops of hydrochloric acid it ought to vanish absolutely. Water which answers to this test in a satisfactory manner is registered as sufficiently free from poisonous metals; and water which does not, is to be condemned as contaminated with metallic impurity.

If a more delicate testing for the above metals be required, such may obviously be accomplished by making a preliminary

concentration by evaporating the water before adding the sulphuret of ammonium; and on this subject nothing need be said, except that the evaporation is generally unnecessary, and that when it is resorted to the water should *not* be evaporated down either in a platinum dish, or in a vessel of lead-glass, but always either in a vessel of hard German glass, or else in a porcelain dish.

It occasionally happens that it is requisite to test a drinking-water for arsenic. This is done by concentrating, and afterwards introducing the concentrated water into a Marsh's apparatus, and looking out for the arsenical spots and rings.

Marsh's apparatus is a small apparatus for generating hydrogen, the exit-tube being armed with a small drying-tube containing chloride of calcium, and narrowed at its extremity, so as to permit of the hydrogen being burnt as it escapes. It consists of a small flask or bottle, containing fragments of pure zinc and some water. Through the cork, which closes the flask or bottle, a funnel-tube is passed, and also an exit-tube bent at right angles. Before being employed in testing for arsenic, it is absolutely necessary to prove that no arsenic is contained by the apparatus. This is done by pouring some sulphuric acid through the funnel into the apparatus, whereby the generation of hydrogen will be caused, and afterwards testing the hydrogen gas for arsenic as it escapes through the exit-tube. The testing of the gas for arsenic is managed by holding a piece of white porcelain in the hydrogen flame, which will deposit the well-known brown arsenical spot on the porcelain if arsenic be present. A still more delicate manner of testing for arsenic, is by heating the glass-tube through which the gas is issuing, when

the presence of arsenic will be manifested by the deposit of a ring of metallic arsenic inside the tube, and just a little in advance of the hot part of the tube. In working with the Marsh's apparatus, care should be taken to avoid explosions; for if the hydrogen be lit prematurely, before all the air in the apparatus has been displaced, there is danger of the well-known explosion by reason of sudden ignition of a mixture of hydrogen and air.

If the Marsh's apparatus show no arsenic when submitted to the testing just described, the concentrated water to be tested for arsenic may be introduced, and the hydrogen again tested for arsenic, as has been described.

Barium.—It is sometimes well to test for this metal, which, however, cannot be present in any waters containing the least traces of sulphates. The testing is very simple: the water is to be concentrated, and then treated with a few drops of dilute sulphuric acid, which will cause a white precipitate or turbidity if barium be present. The water-residue should also be examined as to the colour which it imparts to the flame, and the greenish barium-flame looked out for. It should also be borne in mind that lead also forms a white insoluble sulphate, which should not be mistaken for sulphate of baryta.

Zinc.—Occasionally this metal should be looked for in water. The method of detection depends on the peculiarity of zinc-compounds yielding a solution when treated with excess of potash or soda, and upon this alkaline solution yielding white sulphuret of zinc when treated with sulphuretted hydrogen.

Manganese.—This metal occurs sometimes in river-water, into which manufacturers of bleaching-powder have discharged

their refuse. A case in point came under my observation a few years ago in the north of England. This metal, in very minute quantities, is probably without much action on the animal economy, and at any rate we know of no action which it is said to exert. Manganese is detected in drinking-water as follows:—

A considerable quantity of the water is concentrated by evaporation, and then nearly neutralised by means of hydrochloric acid, and treated with a few drops of solution of peroxide of hydrogen (which may now be bought in London). The formation of a brown precipitate of peroxide of manganese is the sign of the presence of manganese. The test is very delicate. Having obtained the oxide of manganese as a precipitate, it is easy to convert it into green manganate of soda by ignition with a little carbonate of soda and nitre.

Chromium.—It may occasionally be necessary to look for traces of chromium, inasmuch as chromium-compounds are very poisonous, and may possibly occur in drinking-water. In order to test for chromium, a large volume of water should be evaporated to dryness and ignited, the residue may then be boiled with a little dilute hydrochloric acid and a few drops of solution of sulphurous acid. That having been done, the solution should be boiled with a slight excess of ammonia, which will precipitate any trace of chromium in the form of sesquioxide of chromium along with any oxide of iron that may happen to be present. The precipitate may be ignited with a little carbonate of soda and nitre, in order to give the characteristic yellow chromate of soda.

Separate detection of Copper and Lead.—The testing for these metals conjointly has been given above, and, as aforesaid, it usually suffices to make out whether either or both

are present or absent; and the water-analyst may usually be content when he has settled that question. Occasionally, however, it will happen that the separate detection of these metals is required. Copper may be detected by evaporating to dryness a large volume of water, rendering slightly acid with hydrochloric acid, and precipitating with sulphuretted hydrogen. The precipitate is then to be got on a small filter, the filter burnt in a platinum crucible, and the resulting ash heated strongly with a drop of oil of vitriol, which will form sulphate of copper. On cooling this is to be diluted with a few drops of water, and mixed with a few drops of ammonia, which will give the well-known purple-blue colour. A further step to be taken is to evaporate off the excess of ammonia, and then to add a drop of solution of yellow prussiate of potash, which will give the red-brown ferrocyanide of copper. This last reaction for copper is excessively delicate—so much so, that even when the purple-blue given by ammonia may be inconspicuous, the red-brown ferrocyanide is often strikingly visible. When it is neatly and properly executed, this testing for copper is extremely delicate and satisfactory. *Lead* may be detected by forming the iodide of lead. From a large quantity of the sample of water, previously concentrated, the lead is first obtained in the form of sulphuret. The sulphuret is got on a filter paper, and ignited in a little porcelain crucible. The residue is treated with a few drops of nitric acid, and evaporated gently. A few drops of water and a very little iodide of potassium are added, when the yellow iodide of lead will be formed.

Touching the quantities of poisonous metals to which poisoning has been traced in drinking-water, there is the very well-known instance of the poisoning of several members of

the Orleans family at Claremont. In this instance, Hofmann found one grain of lead in a gallon of the drinking-water, and the poisoning was of a very marked and extraordinary description, as is related by Dr. H. Gueneau de Mussy, in the *Dublin Quarterly Journal of Medical Science*, May 1849 (No. XIV., p. 420). There can, moreover, be little doubt that dangerous consequences should be looked for from so small a proportion of lead as one-tenth of a grain per gallon of drinking-water.

As to the circumstances under which lead is to be sought, as has been already said, no analysis of water for sanitary purposes is complete without a search for lead in the very simple manner described above; and one-tenth of a grain per gallon should cause the rejection of a water.

The water of mountainous districts, especially where metals abound, as in Cumberland and Derbyshire, should be very carefully searched for metals. In deciding upon the water-supply to a town, the question of the possible presence of poisonous metals assumes great importance, since it is by no means certain that filtration is capable of removing such impurities.

In this respect metallic contamination forms the most fatal of all objections to drinking-water, and is far more difficult to remedy than organic contamination, which may be got rid of completely by proper filtration.

London has, perhaps, had a most fortunate escape in the collapse of the great scheme for bringing water to it from the lake district of Cumberland.

CHAPTER VII.

THE DRAWING UP OF REPORTS.

As has been already indicated, the proper kind of analysis of potable water, which is generally suitable for sanitary purposes, comprises determinations of solids, chlorine, free ammonia, and albuminoid ammonia, and whether or not the water contains less than one-tenth of a grain per gallon of lead and copper, and whether there is more than the least trace of iron. These data having been provided, a judgment may be pronounced as to whether the water is fit for domestic use or not.

The rules for coming to such a judgment are tolerably simple. Unless the water contain more than 40 grains of solids per gallon, no exception need be taken to the solids as such.

Five or ten grains of chlorine per gallon are not an absolute bar to the use of a water, but only a reason for suspicion under certain circumstances.

If a water yield 0.00 parts of albuminoid ammonia per million, it may be passed as organically pure, despite of much free ammonia and chlorides; and if indeed the albuminoid ammonia amount to .02, or to less than 0.05 parts per million, the water belongs to the class of very pure water. When the albuminoid ammonia amounts to .05, then the proportion of free ammonia becomes an element in the calculation; and I should be inclined to regard with some suspicion

a water yielding a considerable quantity of free ammonia along with more than .05 parts of albuminoid ammonia per million.

Free ammonia, however, being absent, or very small, a water should not be condemned unless the albuminoid ammonia reaches something like 0.10 per million. Albuminoid ammonia above 0.10 per million begins to be a very suspicious sign; and over 0.15 it ought to condemn a water absolutely. The absence of chlorine, or the absence of more than one grain of chlorine per gallon, is a sign that the organic impurity is of vegetable rather than of animal origin; but it would be a great mistake to allow water highly contaminated with vegetable matter to be taken for domestic use.

Drinking-water falls into three classes according to the degree of organic purity, as follows:—

Class I. Water of extraordinary organic purity, yielding from .00 up to .05 parts of albuminoid ammonia per million. This class comprises the most carefully-prepared distilled water and highly-filtered waters, both *natural* (*i.e.*, deep spring waters) and *artificial*, *i.e.*, such water as has passed through a "silicated carbon filter" in good working order. Occasionally a river-water, in its unfiltered condition, falls into this class. Water of this class cannot be objected to organically.

Class II. comprehends the general drinking-waters in this country. It gives from 0.05 to 0.10 parts of albuminoid ammonia per million. I believe that any water falling fairly into this class is safe organically.

Class III. comprehends the dirty waters, and is characterised by yielding more than 0.10 parts of albuminoid ammonia per million.

Date.	Name and Description of the Samples of Water.	Grains per Gallon.		Parts per Million.		
		Solids.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Oxygen consumed in moist combustion.
	LONDON WATER SUPPLY (Thames).....	18.5	1.2	0.01	0.06	2.30
	,, ,, ,, New River.....	17.7	1.1	0.00	0.06	2.48
	,, ,, ,, Kent Company.....	26.5	2.1	0.01	0.02	0.48
	Very bad Water. Thames Water at London Bridge.....	Not determined.	Not determined.	1.02	0.59	Not determined.

PART II.

SPECIAL ANALYSIS, ETC.

CHAPTER I.

THE SPECIFIC GRAVITY OF NATURAL WATERS.

NATURAL waters, which are solutions of different strengths of various substances, must of necessity differ in specific gravity. Ordinarily the difference in specific gravity between one drinking-water and another drinking-water is so small as to be inaccessible to ordinary experiment; and it is only by help of special devices that these differences in specific gravity can be experimentally demonstrated.

I do not recommend that a determination of specific gravity should be commonly made by the chemist when he undertakes a "complete" analysis of a water; and indeed part of the lesson to be learnt in this chapter is, that in general a determination of specific gravity is of little utility, but that in very special cases valuable information may be extracted from it.

In order to fix the subject clearly before the mind, let us take examples. London water with its 20 grains of solids per gallon, Bala water with its 3 grains, and distilled water with no solids per gallon — how will these differ in specific gravity?

It is conceivable that the gallon of water, and the 20 grains of solids in London water, might occupy the same volume after solution as they do when the water and solids are separate. That is one extreme assumption, and, as a matter of fact, is not the truth.

On the other hand, it is conceivable that the gallon of water may take up into solution the 20 grains of solids, and that during solution contraction may occur, so that, solution having been accomplished, the gallon of water and the 20 grains of solids may occupy the space of the gallon of pure water. This assumption is extreme in the other direction, and the truth is included between the two assumptions. Assuming the utmost contraction to take place during solution, we shall get for the specific gravities—

London water	1.00030
Bala water	1.00004
Distilled water	1.00000

and the differences in specific gravity so exhibited must exceed that which can take place in virtue of 20 grains of solids per gallon, 3 grains per gallon, and zero per gallon.

Thus it becomes manifest that the differences in specific gravity presented by ordinary drinking-waters are small figures in the fourth and fifth decimal place; and under ordinary circumstances, the experimental error affecting determinations of specific gravity is a figure (and not always a small figure) in the fourth decimal place.

As is well known, the experimental error in determinations of specific gravity depends upon the difficulty of keeping the liquid exactly at any known temperature; and if this difficulty were got over, our vessels, weights, and balances are good enough to admit of results true within a small figure in the fifth place.

I have recently sought to evade this difficulty. I am content to know the temperature only approximately—say to within one degree centigrade—but I secure that the liquid to be experimented upon, and the distilled water with which it

is to be compared, shall have absolutely the same temperature. This may be accomplished by keeping them for some time in thin flasks, immersed in the same large volume of water contained in a large vessel. Operating in this manner, I have recently obtained the following results at 18° centigrade :—

Sp. gr. of	Distilled water . . .	1.00000
„	Bala water	1.00020
„	London water (West Middlesex Co.)	1.00041

As will be observed, the differences between the specific gravity of distilled water, and the specific gravity of Bala and London water, are larger than can possibly be due to the solids dissolved in these waters. Whence this discrepancy? I have not yet repeated these experiments a sufficient number of times to acquire great confidence in the results, but I do not altogether attribute the discrepancy to experimental error. I attribute the difference in specific gravity to the effect of the solution of carbonic acid and air. The London water and Bala water contain air and carbonic acid in greater quantities than the distilled water, and in virtue thereof are of higher specific gravity than distilled water.

The question as to air I have not yet examined experimentally; but the effect of carbonic acid in raising the specific gravity is shown in the following experiment :—

Distilled water at 21° cent. was charged with washed carbonic acid, and the relative specific gravities taken as above.

Sp. gr. of	Distilled water . . .	1.00000
„	Distilled water containing CO_2	1.00024

This experiment is interesting in another direction. I made quite sure that the water was pretty well saturated with

carbonic acid, for I tested the solution by mixing it with strong baryta-water. If the water was quite saturated with carbonic acid, something like two grammes of carbonic acid should have been taken up by a litre of the water. The experiment shows, therefore, that water does not take up carbonic acid without expanding in volume; otherwise the specific gravity must have risen to between 1.00100 and 1.00200.

As has been said, between ordinary drinking-waters the differences in specific gravity are too small to be accessible to ordinary methods, but this does not hold good in the case of mineral waters. Sea-water, for instance, has a specific gravity of 1.02.

Besides being increased in density by the presence of foreign substances, water may be affected in the opposite manner; thus ammonia and alcohol diminish the specific gravity of water. In extreme cases of well-contamination it might be desirable to take the specific gravity of the first small distillate yielded by a large volume of the water. Once in my experience I met with well-water containing benzol, and, by dint of distillation and redistillation, got evidence of the fact; and, in like cases, I should strongly recommend the making of a careful determination of the specific gravity of the ultimate first distillate. Traces of acetone, alcohol, &c., might be recognised in that manner.

CHAPTER II.

THE WATER-RESIDUE: THE INSOLUBLE SOLIDS: THE SOLUBLE SOLIDS: THE DEGREE OF ALKALINITY.

When a detailed analysis of the solids dissolved in water is to be made, it is desirable to evaporate more than 70 c. c. to dryness. For many purposes it will be found convenient to take 700 c. c., which, as will be observed, admits of returning results in grains per gallon without involving any calculation. Since 700 c. c. of water weighs 70,000 centigrammes, 700 c. c. constitutes a miniature gallon wherein the centigramme corresponds to the grain.

In taking the water-residue for the purposes in view in this chapter, let 700 c. c. be measured and evaporated in a platinum vessel capable of holding 200 c. c., without being full to within a quarter of an inch of the margin of the dish. At first the evaporation may be managed over the naked flame of the lamp, and it will be found convenient to begin by placing 200 c. c. of the water in the dish, and boiling down to 100 c. c., then to fill up and evaporate, and so on until the original 700 c. c. are reduced to 100 c. c. The last 100 c. c. (which contains all the solids of the original 700 c. c.) is to be evaporated to dryness in the water bath, and the dish with adherent residue is finally to be heated in the air-bath to 150° cent., cooled and weighed.

On subtracting the weight of the empty dish (which should

not much exceed 100 grammes), the weight of the dry water-residue from the 700 c. c. is ascertained.

The next point is the division of the water-residue into insoluble residue and soluble residue.

For this purpose small quantities of distilled water (20 c. c. at a time) are successively put into the dish and heated to boiling, so as to dissolve out the soluble part of the residue, and afterwards filtered through a small filter. Care is taken to rub the residue in the dish with a little piece of india-rubber attached to a glass stirrer, so as to insure contact between every particle of solid residue and the water employed to extract the soluble portion. With proper management it is generally practicable to make 70 c. c. of distilled water perform complete extraction of the soluble part of the residue. The solution of the soluble part of the residue is to be evaporated to dryness in a platinum dish, dried at 150° cent. and weighed.

Thus these data are got:—

Total residue from a water . . . .
Soluble residue from a water . . .

The difference between the total residue and the soluble residue is the insoluble residue.

The next points to be considered are, what substances will constitute these two portions of the residue.

The soluble residue will consist mainly of the salts of the alkalies and of salts of magnesia and sulphate of lime

The insoluble residue will contain the carbonate of lime and, in very many cases, hardly anything except carbonate of lime. The high insolubility of carbonate of lime in water absolutely devoid of carbonic acid, insures that the carbonate

of lime shall be left in the insoluble residue in preference to carbonate of magnesia.

This has been made the subject of study, both by analysis of the insoluble and soluble residues, and by synthetical experiments where salts of calcium and carbonate of magnesia being taken, treated with water and evaporated to dryness, carbonate of lime is subsequently found as the insoluble residue. And this general thesis may be deemed to be established:—If the water-residue contains less carbonic acid than can saturate the lime, then the insoluble residue will contain all the carbonic acid combined with lime; and if a water-residue contains more carbonic acid than can saturate the lime, then the insoluble residue will contain all the lime united with carbonic acid.

Besides carbonate of lime, the insoluble residue appears to contain the small portion of silica present in drinking-waters. Any trace of alumina, or phosphate of alumina, peroxide of iron, or phosphate of lime, will be found in the insoluble residue. Carbonate of magnesia may occasionally be found in the insoluble residue, and this will occur in cases in which there is more carbonic acid than is required to saturate the lime.

When a water contains sulphate of lime and carbonate of lime, the sulphate of lime will pass into the soluble residue with great facility; and unless there be more than 14 grains of sulphate per gallon of water, it will not be necessary to employ more than 70 c. c. of water in order to extract the soluble residue. If, however, there be much more than 14 grains of sulphate of lime in a gallon of the water, then the quantity of water employed in extracting the soluble residue must be increased to the necessary amount.

Alkalinity of Water.—Carbonate of lime, which occurs so often in natural water, gives to the water the property of neutralising acids; that is to say, it renders the water alkaline. The degree of alkalinity of water thus becomes a datum of considerable value to the water-analyst.

The degree of alkalinity of water admits of being taken by the employment of the well-known methods of alkalimetry.

There is, however, some practical difficulty in the use of litmus as the *indicator*, since carbonic acid masks the indication, and since litmus is not delicate enough to admit of operation on the water itself without preliminary concentration by evaporation.

If the dry residue be got from a considerable volume of water, and if "decinormal" acid be applied to the water-residue, if the carbonic acid be expelled by boiling, and if the point at which litmus just becomes permanently red be observed, it is possible to determine the alkalinity of water by means of litmus. The operation is, however, very tedious if litmus be used.

A great improvement has been recently made by Professor Mohr, who substitutes cochineal for litmus, and thereby renders the taking of the degree of alkalinity one of the quickest and easiest of all the operations in water-analysis. I am indebted to a private communication from Professor Mohr for the details of the process, and have adopted it in my own laboratory, and made much use of it.

In order to measure the alkalinity of a water, the following is the method of procedure:—

"Decinormal" sulphuric acid having been prepared by taking 4.9 grammes of real H_2OSO_3, and diluting it with

water up to one litre, it will be understood that two cubic centimeters of this decinormal acid will saturate ten milligrammes of carbonate of lime.

If then 700 c. c. of the water be employed for the titration, every two c. c. of the test acid will correspond to one grain of carbonate of lime per gallon of the water.

A solution of cochineal is prepared by bruising the dried commercial cochineal, and digesting it with water, which is gently heated, for a short time. To the solution of cochineal a little alcohol is added, and the whole is filtered, and the filtrate is then fit for use.

The titration itself is a very simple operation. Into a bottle of colourless glass, or a flask, or a large beaker, 700 c. c. of the water is placed; a few drops of the solution of cochineal are then added, and the decinormal acid is measured in, and the point where the violet-red changes to yellow is read off.

The following particulars respecting cochineal are worthy of attention.

In alkaline solution cochineal (carminic acid) is red, or violet-red. In acid solution it is yellow, or brown-yellow. Unlike litmus, it is unaffected by the presence of carbonic acid. It is exceedingly delicate in its indications—so much so, that acid equivalent to one grain of real carbonate of lime in one gallon of water causes the change of colour from decided red to decided yellow. It should also be mentioned that the exact quantity of cochineal employed in the titration is of little or no importance, the indications being equally sharp with very little colouring matter, and with a comparatively great depth of colour. If the operator prefer it, he may use only 70 c. c. of water instead of the 700 c. c.

recommended, and in that case, 0.2 c. c. of acid will correspond to one grain of carbonate of lime per gallon.

The alkalinity having been taken, it will, in a large class of instances, be observed that the alkalinity expressed as grains of carbonate of lime per gallon is almost identical with the *insoluble solids*, being as a rule slightly smaller in amount. Thames water, as supplied by the London companies, is a case in point.

My analysis of Thames water (West Middlesex Co.), date April 1876, showed—

	Per Gallon.
Insoluble solids	13.2 grains.
Soluble solids	6.1 „

The alkalinity taken in August 1876, and expressed in grains of carbonate of lime per gallon, amounted to between 12.0 and 12.5 grains per gallon. Theoretically, the insoluble residue in the case of the London water should slightly exceed the alkalinity, since, in addition to the carbonate of lime, there is a little silica in the insoluble solids.

In those cases where carbonate of soda occurs in water, as often happens in water from the coal-measures and from the clay, the alkalinity may be greatly in excess of the insoluble solids.

The presence in certain waters of carbonates of the alkalies may be proved by the observation that the degree of alkalinity exceeds the degree of hardness; and a knowledge of the alkalinity, conjoined with a knowledge of the degree of hardness and of the quantities of soluble and insoluble solids, affords a tolerably good insight into the constituents of the water.

CHAPTER III.

HARDNESS.

It is matter of the commonest observation that the water in different places differs in hardness or softness. It is hard if much soap be required in order to make a lather, and soft if little soap be required. These differences depend upon the presence of compounds (generally lime or magnesia—salts) which decompose the soap. The more lime or magnesia in the sample of water, the more soap a given volume of the water will decompose so as to give insoluble oleate, palmitate and stearate of lime or magnesia; and consequently the more soap must be added to a gallon of water in order that the necessary quantity of soap may remain in solution, so as to give rise to the phenomenon called lathering.

Many years ago the late Dr. Clark brought out a simple method of measuring the degree of hardness of different waters. He ascertained, by direct trial, how many measures of a standard solution of soap were required by a gallon of water in order to form a lather. Nothing could be more simple or more direct than Dr. Clark's soap-test in itself, but unfortunately an unhappy mode of registering the results was adopted, and a certain degree of confusion crept into this transparently simple matter.

Instead of registering the degree of hardness of a water as

the number of measures of standard soap solution consumed in producing a lather, he registered the degree of hardness as the number of grains of carbonate of lime (or its equivalent of other soap-destroying salts) in the gallon of water.

That a certain definite quantity of soap—and not an infinitesimally small quantity—must be required by a gallon of distilled water in order to produce a permanent lather, is a perfectly obvious fact when it is pointed out. This fact was, indeed, recognised by Dr. Clark, who, although aware of it, had not realised all its consequences, and has thereby fallen into a little confusion.

Since the first edition of this book was written, we have adopted the perfectly direct and simple method of registering degrees of hardness. The relative degrees of hardness of two waters are, on our scale, simply the number of soap-measures consumed by a gallon of the waters in yielding a permanent lather; and the quantity of soap in one soap-measure is the quantity required to precipitate one grain of carbonate of lime.

A gallon of water is an unwieldy quantity to work with. We therefore (and Dr. Clark did similarly) employ, in practice, a much smaller volume, and a correspondingly small fraction of the grain of soap in the measure of standard soap solution. We take our miniature gallon, viz., 70 c. c. of water. This, as has been often explained, contains as many milligrammes of water as there are grains in a gallon. Our standard soap solution is made to contain exactly sufficient soap in one cubic centimeter to precipitate one milligramme of carbonate of lime. When, therefore, we use the miniature gallon, and a certain number of cubic centimeters of standard

soap solution, it is as if we had taken an actual gallon of water, and tested it with a certain number of measures of standard soap solution, whereof each measure contained soap equivalent to one grain of carbonate of lime.

The operation of measuring the degree of hardness of water is very simple.

Into a stoppered bottle (capacity about 200 c. c., but exact size of little importance), which has been cleaned and rinsed with distilled water, 70 c. c. of the sample of water is to be poured. The stopper is put into its place, and the bottle is shaken up. That having been done, the standard soap solution is to be measured into the water by means of a burette or pipette graduated into cubic centimeters. After each addition of the soap solution, the bottle containing the water is to be shaken up, and the point is by and by noted when a lather forms.

In order to observe the formation of the lather, the bottle should be laid on its side; and the lather, to be satisfactory, must be capable of *persisting* for five minutes.

In practice, if nothing be known about the degree of hardness of the sample, it will be found to be most convenient to run in the soap solution boldly, 5 c. c. at a time, and make out approximately and rapidly the degree of hardness of the water. Having done so, in a second more careful experiment the soap solution is at once run in almost up to the required quantity; and then small additions of the soap solution are carefully made, and the exact state of the lathering carefully observed after each addition.

In this manner the taking of the degree of hardness is easily and rapidly accomplished.

In cases of very hard water, when the hardness exceeds

16 degrees, a dilution with distilled water is required, in order that the lathering may take place regularly. If, then, after the addition of 16 c. c. of the soap solution no lather be formed, 70 c. c. of distilled water must be poured into the bottle, and the addition of the standard solution proceeded with. But afterwards, in writing down the degree of hardness, an allowance of one degree must be made for the addition of the 70 c. c. of distilled water.

Another method of effecting the same object is by diluting a hard water with once, twice, &c., times its volume of distilled water, and then titrating the diluted water by means of the standard soap solution. And in such cases the number of cubic centimeters of soap solution must be multiplied by two, three, &c., as the case may be.

The reason why this dilution is called for appears to be that too large a proportion of insoluble lime-salts interferes with the lathering. The rule is, therefore, that water must be diluted appropriately, so that 70 c. c. should never take more than 16 c. c. of soap solution.

Preparation of the Standard Solution of Soap.—I have met with a very convenient soap for this purpose. It is castile soap, and is described as containing 60 per cent. of olive oil. It is now abundant in London. If 10 grammes of the soap be dissolved in a litre of weak alcohol, it yields a solution containing exactly sufficient soap in one cubic centimeter to precipitate one milligramme of carbonate of lime. The standard soap solution is therefore prepared by dissolving 10 grammes of this kind of soap in a litre of weak alcohol, which may conveniently be of about 35 per cent. in strength. Care must of course be taken to dissolve all the soap.

The strength of the standard soap solution may be verified by means of a solution containing a known quantity of carbonate of lime, or of chloride of calcium equivalent to a known quantity of carbonate of lime.

This may be prepared as follows:—1.11 gramme of pure fused chloride of calcium is dissolved in a litre of water. This solution contains chloride of calcium at the rate of one milligramme of carbonate of lime in one cubic centimeter.

Or, one gramme of finely powdered marble, or pure carbonate of lime, may be carefully dissolved in slight excess of dilute hydrochloric acid, and the excess of acid may be neutralised by a slight excess of ammonia, and the whole diluted with pure water so as to occupy the volume of one litre.

In order to verify the soap solution, a number of cubic centimeters of this standard solution of lime—say 12 c. c.—is to be put into the 70 c. c. measure, and filled up to the 70 c. c. mark. In this way 70 c. c. of water are made to contain lime equivalent to 12 milligrammes of carbonate of lime. The 70 c. c. of distilled water itself consumes soap equivalent to one milligramme of carbonate of lime in forming a lather. Therefore this 70 c. c. of solution is equivalent to 13 milligrammes of carbonate of lime, and should consume exactly 13 c. c. of the standard soap solution.

Should the soap solution not be of right strength, it must be made either stronger or weaker until it is correct in strength.

The following determinations of hardness may be cited. They have all of them been made with my own solutions:—

Date. 1874.		Degrees of Hardness.
March 4.	London, New River Co. . . .	15.0
„ 27.	London Thames Co. . . .	16.5
1873.	Leek town-water	3.8
„	Leek Workhouse Well . . .	5.2
„	Oxton, Birkenhead	11.9
„	Chelmsford, Essex, town-water .	13.3
„	Cockermouth, Cumberland . .	2.5
„	Kirby Shore, Westmoreland . .	25.0
„	Chatham	24.0
„	Darley Dale, Derbyshire, Well .	7.5
1876.	Manchester water	3.0

These hardnesses are, as has been explained, the relative volumes of standard soap solution destroyed by a gallon of water in producing a permanent lather.

Suppose the question to arise, How much carbonate of lime is contained by a gallon of one of these waters? the answer is found by subtracting one degree (which is due to the gallon of water itself). Thus, New River water contains 14 grains of carbonate of lime, or else other salts equivalent to 14 grains of carbonate of lime. The Cockermouth water contains only 1.5 grains of carbonate of lime, or salts equivalent to 1.5 grains of carbonate of lime, in the gallon.

All the above determinations are what are called determinations of total hardness. If a water charged with carbonate of lime be boiled, the excess of carbonic acid escapes, and there is deposit of more or less carbonate of lime: and consequently the water becomes softer. The hardness of the water after this deposit is termed the *permanent* hardness, and the difference between the two is termed *temporary* hardness.

Some chemists are in the habit of attaching much importance to these subdivisions of the total hardness, and devote

much trouble to making the determinations. My experience has led me to discard them altogether. Unless great care and judgment be exercised, they are illusory; and the information sought through them is far better and easier to attain in other ways.

Attempts have been made by chemists to utilise the soap-test very widely, and to make, by means of it, something like a complete analysis of the mineral solids in waters. Nicholson, for instance, attempted something of this kind some years ago. No very great success has attended those efforts, except, perhaps, in the case of magnesia, which now admits of very ready and fairly accurate titration by the soap-test.

In my own laboratory I am in the habit of determining magnesia as follows:—

Powdered oxalate of ammonia is added to the water, in the proportion of about one gramme of the oxalate to one litre of the water, and the water with the oxalate in it is shaken up for about a minute and filtered.

The absence of free acid is insured in the filtrate, which is likewise tested with a little oxalate, so as to make sure of the removal of the lime. That having been done, 70 c. c. of the filtrate are titrated with the soap-solution in the usual manner, and if there be any degree of hardness beyond the one degree required by pure water, magnesia is present. The quantity of magnesia may be calculated by measuring the hardness after addition of oxalate (as just described), subtracting one degree and multiplying the remainder by the fraction $\frac{4}{7}\frac{2}{5}$, which will give the quantity of magnesia in terms of carbonate of magnesia per gallon of water.

In order to understand the indications of the soap-test the following facts are useful:—

The presence of numbers of alkaline salts, such as carbonates and sulphates of potash or soda, does not harden the water, but rather tends to soften it, strong solutions of these salts in distilled water being rather softer than distilled water; that is to say, causing a lather to form with a smaller quantity of soap-solution.

Dilute solutions of these salts, and also dilute solution of oxalate of ammonia, have no sensible effect on the indication of the soap-test.

Lime and magnesia solutions behave very differently towards solutions of soap. Lime reacts immediately and forms oleate, palmitate or stearate of lime, and accordingly the lime-hardness is instantly observable on employing the soap-test.

Magnesia, on the other hand, does not instantly complete its reaction on soap, but requires the lapse of time. When the reaction of magnesia on soap is finished, another very singular peculiarity manifests itself, viz., that one equivalent of magnesia consumes as much soap as one and a half equivalent of lime—hence 75 degrees of hardness count for 42 grains of carbonate of magnesia per gallon.

The following experiment is instructive, and serves to illustrate what has just been advanced:—

Let a water containing 4.2 grains of carbonate of magnesia per gallon be operated on with standard soap-solution. Having added, say 4 c. c. of soap-solution to 70 c. c. of this water, a partial lather will be observed on first shaking up, but on shaking up a second time no lather will form. On adding, say up to 6 c. c., a tolerable lather may be obtained at first, but after standing a little, and after shaking up well a second time, the lather will not form; and up to between 7.5

and 8.5 c. c. of soap-test will be found requisite to get a lather which is quite persistent after repeated shaking up.

With a little practice the water-analyst may soon familiarise himself with the peculiarities of magnesia, hardness; and if he work to a well-formed decided lather, and make allowance of one c. c. for the water (or even more if he work to a very great lather), he may measure magnesia in drinking-water in the space of a quarter of an hour, and do it with fair accuracy.

In my own laboratory I made some experiments on this determination a while ago, and I found that 20 grains of Epsom salts having been dissolved in a gallon of water tolerably rich in lime, and the lime having been precipitated as oxalate as above described, the titration of the magnesia was very accurate.

The importance of being able to titrate magnesia in drinking-water in about a quarter of an hour, becomes manifest when it is considered that the common determination of magnesia is the longest operation in water-analysis, and generally extends over a couple of days or more.

Before taking leave of the soap-test, I ought to mention that standard soap-solution does not keep good for ever. After the lapse of a few months it sometimes suffers strange changes, and deposits a precipitate and loses in strength. It is absolutely necessary, from time to time, to verify the standard soap-solutions; and I believe that serious errors have arisen from the want of knowledge that soap-solution suffers spontaneous change.

CHAPTER IV.

GENERAL QUANTITATIVE ANALYSIS OF THE WATER RESIDUE.

THE following course of analysis may be pursued when a complete mineral analysis of a water residue is required:—

700 c. c. of the water (clear either by decantation or filtration through filter paper) having been measured out, a few drops of pure hydrochloric acid are to be added, so as to render the water distinctly acid. The water is then, by degrees, to be got into the large platinum dish and evaporated, first over the naked flame, and at last in the water-bath, to complete dryness (vide Chapter I. pp. 9, 10). Ultimately the residue may with advantage be heated to 150° Cent.

Next, when it is cool, a few drops of hydrochloric acid are to be added to the residue, and distilled water in considerable quantity (say 50 c. c.) is to be added, and the inner surface of the dish is to be well rubbed either with indiarubber or with the finger previously carefully cleaned and washed. At this stage the *silica* present in the water has assumed the form of a precipitate. The liquid is, therefore, filtered through a small Swedish filter-paper. The precipitate is washed, dried, ignited, and weighed, and is the silica.

The filtrate is next to be rendered alkaline with ammonia, and there precipitates—alumina, oxide of iron, and phosphoric acid combined with those oxides; and, in cases where

there is not enough alumina and iron to saturate all the phosphoric acid, there may be phosphate of lime. As I shall presently explain, phosphates in drinking-water are hardly ever present except as minute traces. The precipitate just described should be separated by filtration, washed, dried, ignited, and weighed.

The filtrate may now be treated with oxalate of ammonia, which precipitates the lime in the shape of oxalate of lime. This is separated by filtration, washed, gently ignited, so as to convert it into carbonate of lime, and weighed.

During this ignition, a small quantity of the oxalate is usually decomposed so as to yield quick-lime, and it is necessary to restore carbonic acid to it. This is done by moistening the cooled precipitate with water in which a piece of carbonate of ammonia has been dissolved, and carefully drying.. The precipitate is then to be heated to approaching redness, cooled and weighed.

In this manner the lime present in the sample of water is obtained as carbonate.

The filtrate contains the magnesia, and is to be concentrated by evaporation, rendered alkaline with ammonia, filtered if necessary, and then treated with solution of phosphate of soda and more strong ammonia. In course of time, double phosphate of magnesia and ammonia is precipitated in the crystalline form. After being allowed to stand for some hours (6 or 12 hours), the solution is filtered in the cold, and the phosphate washed with ammonia-water (strong ammonia diluted with an equal volume of water). The phosphate is then ignited and weighed, and consists of pyrophosphate of magnesia, $PO_5\ (MgO)_2$.

In order to make accurate determinations of magnesia, the

fact of the solubility of ammonia-phosphate of magnesia must be borne in mind and provided for. This is done by taking care to have the liquid, in which the magnesian-precipitate is to be made, very ammoniacal (half of it being strong—sp. gr. 0.88—ammonial liquid), and by measuring the filtrate and wash water, and allowing one milligramme of magnesian phosphate for every 50 c. c. of filtrate or wash water.

When properly done, the determination of magnesia is very satisfactory. It will thus be seen, that from the same 700 c. c. of water we obtain successively :—silica, oxides of iron and alumina, &c., carbonate of lime, phosphate of magnesia. For the other constituents, fresh portions of water are to be taken.

The alkalies, potash and soda, are determined thus :—

700 c. c. of the water is evaporated to dryness in platinum, then some caustic baryta (0.10 gramme is generally sufficient) is put into the dish, and a little distilled water added. The dish with its contents is then carefully heated till the contents boil. They are then filtered, and the filtrate will contain the alkalies in the form of chlorides, nitrates, &c. (but not sulphates), together with some baryta, and possibly lime. A little carbonate of ammonia is used to precipitate the baryta and lime. The liquid is again filtered and evaporated to dryness in a platinum dish. The residue is ignited with exceeding care, to avoid volatilising the alkalies, a little solid chloride of ammonium being used if necessary, and then the alkalies are finally weighed as chlorides.

That having been done, the potash may be precipitated by means of bichloride of platinum, the precipitate may be washed with alcohol, separated by means of a tared filter, dried

and weighed. In this manner, the potash is obtained as chloro-platinate of potash $PtCl_2KCl$. When only traces of potash are present, there is no objection to igniting the precipitate along with the filter paper, and then weighing metallic platinum and chloride of potassium.

I have thus described the common course of complete mineral analysis of the water-residue.

It remains to be observed, that the determination of alkalies may with advantage be made as follows :—

The soluble solids having been weighed, and lime and magnesia having been determined in the soluble solids, the difference between the soluble solids and the lime and magnesia in them is the alkalies.

The Sulphates in Water.—The determination of sulphuric acid in water is very satisfactory and accurate, and is made by the usual method of converting it into sulphate of baryta, and weighing the sulphate of baryta.

For this purpose a convenient quantity of the water (which must be quite clear) is measured off, heated to boiling, and then treated with slight excess of solution of chloride of barium and a few drops of hydrochloric acid, boiled and filtered. The precipitate is washed, ignited, and weighed.

It is not a matter of much consequence whether much or little water be taken for the determination ; two or three hundred cubic centimeters answers very well. I have myself got excellent results on so small a scale as 70 c. c. of water, having, in that case, made a solution of chloride of barium of known strength, and added known volumes of it to the water, taking care always to have excess of chloride of barium, but never very great excess. The importance of having good

filter-paper for this determination is understood by all chemists.

The Chlorides in Water have been sufficiently treated in Part I., and here it is only necessary to remark that by appropriate concentration any desired degree of accuracy is attainable.

The Nitrates in Water are determined by reducing the nitric acid with aluminium foil, in presence of much caustic alkali, and thereby converting it into ammonia, which, if it be little, is measured by the Nessler test, and, if it be much, is measured by alkalimetry.

The details of the operation are as follows:—

First of all caustic soda is prepared quite free from nitrates. This is done by dissolving metallic sodium in water, in the proportion of two grammes of sodium to 100 c. c. of good distilled water.

70 c. c. of the water to be tested is then mixed with an equal volume of the alkali-solution, and a piece of aluminium foil, larger than is capable of dissolving, is placed in it and left for several hours. At the end of the time the liquid is distilled in a small retort, and the distillate Nesslerised.

Very accurate results are attainable by the method when it is efficiently carried out.

In reckoning the quantity of nitric acid from the quantity of ammonia yielded, every atom of ammonia corresponds to an atom of nitric acid.

$$\begin{array}{ccc} NH_3 & : & HNO_3 \\ 17 & : & 63 \end{array}$$

The following examples may be cited:—

	Grains of Nitric Acid (HNO_3) per Gallon.
London Thames Water Co. . . .	1.1
London New River Co.	1.1
London Kent Co. (very pure) . . .	1.3
South Essex Co.	2.7
Guildford, Surrey (very pure) . . .	1.1
Wells in West of England (very pure) .	2.0
Glasgow, from Loch Katrine . . .	0.1
Manchester, from Derbyshire Hills . .	0.0
Bala Lake (a dirty water)	0.0

The nitrates and nitrites have been erroneously regarded as measuring the defilement of water. Nitrogenous organic matters decay and are oxidised, and yield more or less nitrates by the oxidation of the nitrogen which they contain. Reflecting on this fact, some chemists have proposed to regard the amount of nitrates in a water (a small correction having been made for the nitrates existing in rain water) as the measure of the sewage which has been discharged into the water and undergone destruction. The recent reports of the Registrar-General on the state of London water refer to these data as showing "*previous sewage contamination.*"

But if nitrates are generated by oxidation of the organic refuse discharged into water, they also find their way into it from the various geological strata traversed by the water. Chalk springs, which contain no organic matter, are often highly charged with nitrates.

Again, on the other hand, the processes of vegetation in rivers and lakes are calculated to withdraw nitrates from the water.

In fine, presence or abundance of nitrates does not show defilement by means of sewage, and deficiency of nitrates does not show absence of defilement.

Many excellent waters have been condemned as unwholesome on account of the nitrates contained by them: and it cannot too strongly be insisted upon that the nitrates afford no data of any value in judging of the organic quality of a water.

Iodates, Bromates, and Chlorates.—The existence of traces of iodates in natural water deserves to be referred to, inasmuch as conflicting reports as to the finding of iodine in certain waters owe their origin to neglect of this possibility.

In a fully-ærated water iodides are very likely to have undergone oxidation into iodates or periodates. Bromides and chlorides are not so easily oxidised, but even these salts may undergo oxidation. The way to deal analytically with these products is obvious. The water should be acidified with a suitable acid, and then boiled with sulphurous acid in order to reduce iodates, &c., into iodides, &c.

Phosphates.—As has been already mentioned, the phosphates will be found in the precipitate given by ammonia when the acid liquid is rendered alkaline. In order to estimate the phosphoric acid, the precipitate in question, which contains the alumina and iron, should be redissolved in a little hydrochloric acid, and to the solution a few drops of solution of perchloride of iron may be added, and then the solution should be nearly neutralised with ammonia, and lastly, slight excess of acetate of ammonia should be added. In this manner a precipitate containing phosphate of iron and alumina, but devoid of lime and magnesia, is obtained.

The precipitate should be washed, and then dissolved with a little tartaric acid, and to the tartaric acid solution a solution of ammonia-sulphate of magnesia may be added, together with large excess of ammonia. In that manner the phosphoric acid will be obtained in the form of the ammonia-phosphate of magnesia, which may be washed with ammoniacal water, ignited and weighed, and from which the weight of the phosphoric acid admits of easy calculation. I have, however, to remark that—except in almost infinitesimal quantity—phosphates seldom occur in drinking-water; and in order to meet with any success in estimating phosphates in drinking-water, a very large quantity—many litres—should be employed.

Much nonsense has been talked about phosphates in drinking-water; and the fact has been overlooked that, except as infinitesimal traces, they cannot exist along with carbonate of lime in a clear water.

The following experiment may be made with common London water, which holds carbonate of lime in solution. Let a few drops of clear solution of phosphate of soda (which, as will be borne in mind, is really an acid salt) be dropped into a beaker containing bright London water, and presently, on stirring, the well-known precipitate of phosphate of lime will appear. From this result it is manifest that carbonate of lime and phosphates are incompatible in drinking-water.

The mode of stating the results of the analysis of the mineral solids dissolved by drinking-water I look upon as a matter of some importance; and I am even disposed to think that the thing most pressingly called for in connection with

analysis of this description is a reform of the methods of statement.

The method which has come to be fashionable in many quarters is perhaps the most unsuitable that could possibly have been adopted. I refer to the fashion of stating the quantity of each metal and each acid-radical in a given quantity of water. An excellent set of examples of this mode of statement is to be found in Watts's Dictionary, under the heading "Water," and to this excellent set of examples I would refer the reader who desires to know experimentally the disadvantages of the method.

The advantages claimed for the method are, that it makes no hypothesis, but confines itself to bare and rigid affirmation of ascertained facts, that it lends itself to no sort of cookery, and never makes similar waters seem dissimilar, nor like waters appear unlike.

But if the reader will turn to examples—to the examples in Watts's Dictionary, for instance—he will find that the method has the fatal property of masking and concealing most fundamental facts that the analysis should disclose.

If the reader will turn to any of the examples in the table in the dictionary, he may convince himself that simple inspection of the tabular statement of the constituents of the water-residues does not inform him whether the water-residue be neutral, acid, or basic; and in order to discover this most simple and fundamental chemical fact touching the water-residue, the reader must divide every quantity of metal and acid-radical by its equivalent, then add up the two sets of numbers, and note whether the base or the acid-radical predominates.

It appears to me that a proper and suitable mode of statement is that which, on the face of it, exhibits the most fundamental facts; and I think that the old-fashioned plan of distributing acids and bases, so that the strongest acid gets the strongest base, is much to be preferred to the modern fashion above described; and the plan which I propose is the old plan slightly modified to meet the exigencies of the case.

When only one base and only one acid are present, there can, of course, be no ambiguity; and a pure solution of carbonate of lime, or of common salt, could not be better described than as a solution of carbonate of lime of such and such a strength, or a solution of salt of such and such a strength; and solutions where the one salt greatly predominates over all others, may, conveniently and instructively, be looked upon as impure solutions of the one salt. A large class of natural waters contain carbonate of lime, greatly preponderating over everything else, and in sea water (which constitutes by far the largest proportion of natural water) there is an example of a solution containing chloride of sodium greatly preponderating over the other salts.

Water-residues may accordingly be looked upon as impure carbonate of lime, or impure chloride of sodium.

In Chapter II. (page 17) I have brought forward the fact that if a water-residue be washed with a little boiling water, as much of the lime as the carbonic acid will saturate remains behind as the insoluble residue. The adoption of the division of the water-residue into soluble solids, and insoluble solids, falls in quite naturally with the method of statement which I am recommending.

The principle which I recommend is to express as much as possible carbonate of lime, and chloride of sodium, as the analytical data will admit of.

Furthermore, I think it desirable as far as practicable to give the analytical data themselves, and in Part III. will be found numerous examples in illustration of the principles laid down.

CHAPTER V.

GASES AND VAPOURS DISSOLVED BY WATER.

WATER is capable of absorbing, in a greater or less degree, every gas and every vapour which is placed in contact with it.

All water which has been kept in open vessels is necessarily charged with nitrogen and oxygen gases, inasmuch as these gases form the chief constituents of the atmosphere. And if any sample of water be freely shaken up with large volumes of air, it will presently become charged with nitrogen and oxygen in certain well-ascertained proportions, depending on a physical law. A litre of water, freely shaken up with large volumes of air at 15° Cent., will absorb 17.95 cubic centimeters of air, the composition of which is—

Nitrogen	65.1	vols.
Oxygen	34.9	„
	100.0	„

The composition of the dissolved air is governed by the relative proportions of nitrogen and oxygen gases in the atmosphere, and by the coëfficient of absorption of each gas at the temperature at which the absorption takes place. At 15° Cent. (according to Bunsen) the absorption coëfficient of nitrogen is 0.0148, and that of oxygen 0.0299, whilst the relative volumes of nitrogen and oxygen in air are—

Nitrogen	79.0
Oxygen	21.0
	100.0

The relative proportions of nitrogen and oxygen which water dissolves from the atmosphere at 15° Cent. are therefore, according to the law, $.0148 \times 79 : .0299 \times 21$, which gives in percentage—

Nitrogen	65.1 vols.
Oxygen	34.9 „
	100.0 „

If water be taken from rivers and springs, and be bottled up without being freely exposed to the air, it will often be found to exhibit a very different ratio between the dissolved nitrogen and oxygen gases.

Thus, in the autumn of 1859, W. A. Miller found that a litre of Thames water at Woolwich contained 63.05 c. c. of dissolved gases, the composition of these dissolved gases being :—

Carbonic acid . . .	48.3 c. c.
Nitrogen	14.5 „ „
Oxygen	0.25 „ „
	63.05 „ „

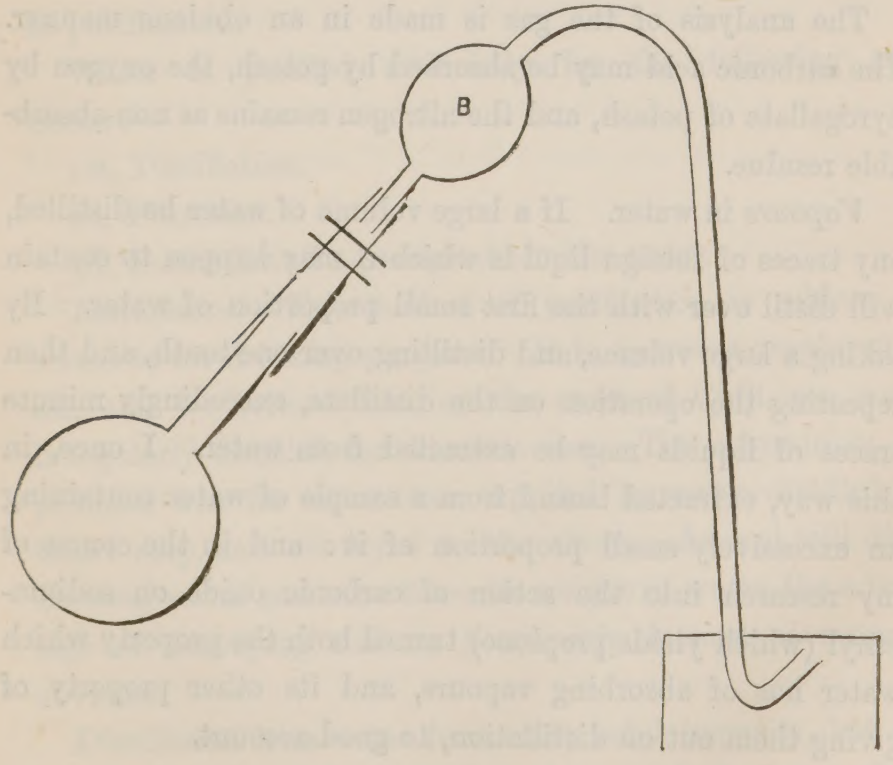
showing extraordinary diminution of the oxygen.

Higher up the river the ratio of nitrogen to oxygen was quite different. Thus, at Kingston, Miller found in a litre of Thames water 52.7 c. c. of gases, consisting of—

Carbonic acid . . .	30.3 c. c.
Nitrogen	15.0 „ „
Oxygen	7.4 „ „
	52.7 „ „

As will be observed, the ratio of the nitrogen to the oxygen in this water is very nearly that which theory requires in a perfectly aërated water.

Undoubtedly the Thames water, taken out of the river at Woolwich, owes its deficiency of oxygen to the reducing action of the urea and other matters poured into the river in the form of sewage. And starting from this fact, an attempt has been made to raise thorough aëration as a sort of standard of purity. Very little practical use can, however, be made of the state of aëration, since the purest deep-spring waters are also liable to imperfect aëration. And in this respect the very best and the very worst waters are on a par with one another.



The gases in water are estimated by taking a known volume of water, boiling out the gases, and collecting them

over mercury. A flask capable of containing about 500 c. c. of water, and provided with a narrow neck, is filled completely with the sample of water under examination. The neck is surrounded with a stout, tightly-fitting vulcanised indiarubber tube (*vide* fig.) The indiarubber tube is pinched by a clasp, and connects the neck of the flask with an exit tube, on which is blown a bulb B. In the bulb B is placed a little water. The operation is commenced by boiling the water in the bulb B, so as to clear the bulb and exit-tube of air. That having been done, the clasp pinching the indiarubber connector is loosened, and the water in the flask is then heated till it boils and has liberated all the gas, which is collected and measured over mercury.

The analysis of the gas is made in an obvious manner. The carbonic acid may be absorbed by potash, the oxygen by pyrogallate of potash, and the nitrogen remains as non-absorbable residue.

Vapours in water. If a large volume of water be distilled, any traces of foreign liquids which it may happen to contain will distil over with the first small proportion of water. By taking a large volume, and distilling over one-tenth, and then repeating the operation on the distillate, exceedingly minute traces of liquids may be extracted from water. I once, in this way, extracted benzol from a sample of water containing an excessively small proportion of it: and in the course of my research into the action of carbonic oxide on sodium-ethyl (which yields propione) turned both the property which water has of absorbing vapours, and its other property of giving them out on distillation, to good account.

CHAPTER VI.

PURIFICATION OF WATER.

WATERS contaminated with animal and vegetable matters are purified in nature by the decomposition and oxidation of their organic matter, aided by subsidence, and by filtration through porous strata. The processes of evaporation and condensation which give rise to rain are also natural methods of purification.

Water is purified artificially by the following processes:—

1st, Distillation.

2d, Filtration.

3d, Formation of a precipitate in the water.

Distillation.—This method of purification is seldom resorted to for drinking purposes. It is, however, employed at sea, and we believe that, on the coast of Chili, sea water is regularly distilled for domestic use. The Abyssinian expedition was for some time supplied by water distilled on board ship, and conveyed to the shore. As coal will distil between seven and nine times its weight of water, the advantage of conveying coal on board ship instead of water is obvious.

Distillation frees water from every solid impurity, but not from ammonia, carbonic acid, and any volatile bases which may be present. By rejecting the first part of the distillate,

therefore, which contains most of the impurities, we obtain water free from everything except the traces of organic bases, ammonia, &c., which may be generated from the solid organic matter during the distillation. Perhaps the best method of obtaining pure from common water is to redistil distilled water with a little potash and permanganate of potash, and reject the first portion of the distillate. Such water will be quite free from ammonia, carbonic acid, and organic matter. It will contain air, and perhaps traces of matter dissolved from the condenser. Glass dissolves to a very minute extent, if used as a condenser. Silver is said not to do so; nor has it been observed that a copper condenser communicates any solid matter to distilled water.

Distilled water is flat, and to most people unpalatable; but we know from experience that some people get accustomed to it, and prefer it to all other waters. It, to a great extent, loses its unpleasant flavour if exposed to the air for a few hours.

Filtration.—This is the most common method of purifying water. If a water contains solid particles of a given magnitude, and we pass that water through a wire gauze, the meshes of which are of smaller diameter than the particles, we shall, of course, separate the particles; and unless either the gauze or the particles are elastic, the rate at which the operation is conducted will have no effect on the result. But in filtration, as ordinarily conducted, speed affects the result to a very great extent. In filtering through beds of sand, we may roughly say that the effect of the filtration will be almost inversely as the speed at which the filtration is effected.

If a bottle full of slightly turbid water be laid upon its

side, and allowed to stand for twenty-four hours, and then examined, it will be found that the sediment has not only deposited itself on those parts of the glass to which gravitation has carried it, but that, though thickest at the bottom, it has spread itself much higher up, and in many cases is even to be found adhering to the top part of the glass. This circumstance has doubtless much to do with filtration.

There is, however, another consideration which will perhaps be most easily explained by an example. When softening water by Clark's process, we obtain a precipitate of finely-divided carbonate of lime. If this operation be conducted in large glass vessels (three to four gallons), we can watch this process of depositing the precipitate. If we do so, we shall observe that the first sign of clearing takes place at the top, a layer of quite clear water making its appearance, and gradually extending downwards. If we ask how this water has become clear, the only answer that can be made is, that the precipitate has moved down to the layer of water beneath it, and thereby rendered that layer thick; for had the precipitate not descended into it, it would, like the top layer, have become clear. In the same way, this second layer, by its depositing, renders that beneath it turbid. If such a vessel of water took six hours to clear, we should expect that by dividing it into six layers by means of five diaphragms, equidistant from each other and from the top and bottom of the water, that the water would clear in one-sixth the time, or one hour. On making the experiment, this is found to be the case. To test this matter more fully, what may be called a "subsidence filter" was constructed. It consisted of a wooden box 12 inches square and 20 inches deep, containing 24 plates of sheet zinc, $\frac{3}{4}$ inch apart. Each plate had six holes punched

in it, one inch in diameter. The holes were near to the side, and had their edges turned up a little; the plates were so arranged that the holes were not opposite each other. A small tap came from just below the lowest plate. Another box like this, but without plates, was also constructed. Both boxes were charged with freshly-softened water, containing chalk suspended in it. The water took about eight hours to clear in the box without the plates, and was quite clear in the one with the plates at the end of twenty-five minutes. This box of plates was next used as a filter, by sending a slow stream of water charged with suspended chalk through it. About eleven gallons an hour of quite clear water could be drawn off. If the speed was increased much beyond this, the water was no longer clear. To render the analogy between this "filter" acting entirely by subsidence and the common sand filter quite plain, the box without the plates had a piece of coarse wire-gauze stretched across it just above the tap. It was then filled with slate chips (the small splinters produced by breaking and chipping slates), and water containing chalk in suspension, as before, filtered through it. The action of this filter was exactly the same as that of the plate filter, except that more water could be passed through it per hour without turbidity. If, however, more than about fifteen gallons per hour was passed through it, the water was slightly turbid; and if the quantity was increased to twenty gallons, it was quite so. Some experiments, substituting very coarse sand for the slate, gave analogous results.

Now, the analogy between the last experiments and the subsidence filter is clear; and we may safely draw the inference that a portion of the work performed by a sand filter is due to subsidence within the filter itself, the particles of sand

serving as plates. This is almost proved by the fact, that we can force much of the matter removed by such a filter through it, by slightly increasing the pressure of water, which would not be the case if the filter acted as a strainer.

The common process of filtration through sand is therefore an operation comprising three distinct methods of purification.

1st, Straining.

2d, Removal of matters by adhesion to the sand.

3d, Subsidence within the interstices of the filter itself.

The first method will vary with the size of the apertures through which the water passes; the second, with the amount of surface in the filtering medium in relation to the amount of water; the third will vary with the speed at which the water travels, and with the size of the aperture through which it passes.

The following are examples of the effect of this kind of filtration on the organic matter in the water:—

Waters taken from the Thames near Hampton Court, where the Water Companies take their Supply.

	Free. NH_3	Albuminoid. NH_3
I. Water taken above the Weir, and some distance above Hampton Court, July 1867	0.045	0.28
II. Another sample taken below the Weir, July 1867	0.015	0.23
Sample I. filtered through filter-paper .	0.045	0.21
Sample II. „ „ .	0.015	0.185
Sample taken above the Weir in September 1868	0.02	0.22
After the filtration effected by some of the London Companies, this water was delivered in London as follows:—		
July 1867	0.01	0.06
September 1868	0.015	0.07

Some filtering media not only remove organic matter from dilute solutions, but actually destroy it. This they do by causing the oxygen dissolved by the water to combine with the organic matter. Foremost among the substances which possess this property stands charcoal.

I have specially studied the action of a certain kind of prepared charcoal, consisting of one part of mineral matter and two parts of charcoal, and known as the "silicated carbon" of the Filter Company of that name.

This material I find to be endowed with extraordinary powers, as the following experiments show.

Some of the Southwark and Vauxhall water was submitted to analysis, and gave—

	Parts per million.
Free ammonia	0.02
Albuminoid ammonia . . .	0.14

showing that at that rate this water was almost devoid of ammonia, but considerably charged with complex nitrogenous organic matter.

The water was quickly filtered once through a cake of silicated carbon about 4 inches in thickness. The filtrate contained—

	Parts per million.
Free ammonia	0.16
Albuminoid ammonia . . .	0.04

The filtrate was passed three times through the filter, and then it contained—

	Parts per million.
Free ammonia	0.14
Albuminoid ammonia . . .	0.01

With dilute solutions of urine and of milk a similar result—viz., destruction of "complex nitrogenous organic matter,"

and formation of ammonia as a product of the destruction—was observed.

The rate of filtration (and of consequent destruction) was very rapid. I found that 225 c. c. of water passed through the small filter in one minute.

Thus it will be seen that passage through a silicated carbon filter, and boiling with potash and permanganate of potash, have the same effect upon a dilute solution of complex nitrogenous organic matter; both operations decompose complex nitrogenous organic matter, and both operations generate ammonia.

In continuing my investigation into the action of the silicated carbon filter, I have proceeded to experiment on solutions containing a by no means infinitesimal quantity of organic substance, and, as will be apparent from the following details, have obtained a very striking result.

In these experiments I employed a rather larger filter than before, viz., a filter containing a cake of silicated carbon six inches in thickness, and the filter was quite new.

Experiment I.—Into a quantity of boiled London water (which yielded 0.00 milligramme of free ammonia and 0.04 milligramme of albuminoid ammonia per litre) I placed a weighed quantity of acid sulphate of quinine. In this manner a large volume of dilute solution of acid sulphate of quinine, of such a strength that one litre contained 14.2 milligrammes of the acid sulphate, was prepared. Before making the experiment with the filter I subjected some of this dilute solution of quinine to the ammonia process, and obtained from 1 litre—

Free ammonia	trace.
Albuminoid ammonia . . .	0.48 milligramme.

The solution was then poured on the filter, care having been taken beforehand to empty out all the water which was in the filter.

The first litre of filtrate was thrown away, inasmuch as I considered that the first litre would consist of water displaced by the solution of quinine. Successive half-litres of filtrate, as they came through the filter, were analysed with the following results :—

	Milligrms. per Litre.	
	Free Ammonia.	Albuminoid Ammonia.
No. 1	0.24	0.04
No. 2	0.14	0.04
No. 3	0.15	0.04
No. 4	0.14	0.02

The circumstance of the low yield of albuminoid ammonia not being confined to the first portions of filtrate, is a demonstration that I had eliminated the influence of dilution by water previously occupying the pores of the filter, and the result may be accepted with confidence that a solution of quinine, which yielded 0.48 m.grm. of albuminoid ammonia per litre, was so purified by a single filtration through six inches of silicated carbon, that after filtration it yielded only 0.04 or 0.02 milligramme of albuminoid ammonia per litre.

Encouraged by this result, I prepared a much stronger solution of quinine, viz., a solution containing 118 milligrammes of acid sulphate of quinine per litre. The acid sulphate of quinine which I employed was in large crystals, and had been previously investigated and found to contain 21.1 per cent. of water of crystallisation. As the reader will observe, the above-mentioned solution contained 8.26 grs. of salt to the gallon of water and such a solution is quite bitter to the taste.

Experiment II.—The above-described solution of quinine (118 milligrammes of acid sulphate of quinine in a litre of water) was passed through the filter, and after rejecting the first litre of filtrate, examinations of the further filtrate were commenced. The filtrate yielded—

Milligrms. per Litre.	
Free Ammonia.	Albuminoid Ammonia.
0.20	0.02

This result was further confirmed by evaporating a quantity of the filtrate down to dryness and weighing and igniting the residue. As will readily be understood, a solution containing as much as $8\frac{1}{4}$ grs. of sulphate of quinine per gallon is strong enough to be dealt with by simple means, and accordingly I experimented in that manner with the solution before and after filtration, and got perfectly satisfactory results. Finally, I tasted the filtrate and found that all bitterness had gone away.

Thus I have arrived at the startling result, that by a simple filtration through six inches of silicated carbon a solution of quinine, containing $8\frac{1}{4}$ grs. of the acid sulphate per gallon of water, is totally deprived of quinine.

A solution of hydrochlorate of morphia in common London water was prepared by taking 1.320 grms. of hydrochlorate of morphia, dissolving it in water, and diluting the solution to ten litres. In this manner a solution containing 0.132 grm. of the hydrochlorate per litre of water was obtained. Submitted to the ammonia process, this solution was found to yield 2.60 m.grms. of albuminoid ammonia per litre. Five litres of this solution were then allowed to run through the same silicated carbon filter which had been employed for the experiments on quinine described on p. 114, and the five litres of filtrate were

then thrown away. In this manner the most ample displacement of the liquid occupying the pores of the filter was insured. About five more litres of the solution were next run through the filter, and the filtrate was examined with the following results :—

Milligrammes of albuminoid ammonia per litre of liquid— No. 1, 0.06 ; No. 2, 0.04 ; showing how completely the filtration had removed the morphia from the solution.

As a further corroboration, advantage was taken of the reducing properties possessed by morphia, which decolourised standard solution of permanganate, and which may be titrated with such a solution.

Before submitting it to filtration, 100 cubic centimeters of the solution of morphia reduced 8.5 c. c. of decinormal permanganate solution.

After filtration, 100 c. c. of the liquid did not reduce any appreciable quantity of the permanganate. Thus it has been proved that one single filtration through a thickness of six inches of silicated carbon is sufficient to remove morphia from a solution containing 132 milligrammes of the hydrochlorate of morphia in one litre of water (or 9.24 grains per gallon).

I next endeavoured to reach the limit of strength capable of being dealt with by these filters. I dissolved 2.739 grms. of hydrochlorate of morphia in three litres of distilled water, thereby getting a solution containing 913 milligrammes of that salt per litre of water (or 63.91 grs. per gallon).

This solution, as will be seen, is capable of decolourising pecinormal permanganate solution at the rate of 59 c. c. of permanganate per 100 c. c. of the morphia solution.

It was poured on a very small silicated carbon filter; the

first half of the filtrate was rejected, and the second half examined. The filtrate was at first found to contain much morphia, but after making it pass and re-pass through the filter, the morphia was so far reduced in quantity that 100 c. c. of the filtrate decolourised only 2 c. c. of decinormal permanganate, showing that about 29.30ths of the morphia had been absorbed by the filter. To attain this result, five or six passages through the filter were required.

Until I break up the filter and weigh the fragments of the cake, I cannot say with accuracy how much silicated carbon has been required to absorb the morphia. Roughly, however, the weight of the cake may be set down as 1000 grms., and, at that rate, 1000 grms. of silicated carbon is capable of absorbing at least two grms. of hydrochlorate of morphia. I propose, however, to make accurate determinations of the extent to which silicated carbon may be loaded with morphia.

In continuing my investigation, I have experimented on a solution of strychnine. In ten litres of London Thames water (West Middlesex Company), which yielded 0.05 milligramme of albuminoid ammonia per litre, I dissolved 1.263 grms. of strychnine, using a little hydrochloric acid (about 5 c. c. of the strong acid) to facilitate the solution.

As will be seen, this solution contains 0.1263 grm. of strychnine per litre, or 8.841 grains per gallon. Such a solution is bitter to the taste. I drank 5 c. c. of it, and found it to be very bitter.

Submitted to the ammonia process, the solution yielded 5.20 milligrammes of albuminoid ammonia per litre.

In making the experiment on the filtration of this solution I desired to ascertain whether or not the silicated carbon

filter preserves its power, and accordingly employed the same filter which had already absorbed quinine and morphia in previous experiments. Already the filter had taken up about 0.7 grm. of acid sulphate of quinine and 1.3 grms. of hydrochlorate of morphia, and since taking up these alkaloids had not had very large quantities of water passed through it. The filter was very carefully drained of water, and then the ten litres of the above-described solution of strychnine placed in it. The first five litres of filtrate were thrown away, and the remainder was collected.

Submitted to the ammonia process, it yielded some free ammonia and 0.04 milligramme of albuminoid ammonia per litre, which shows that the filtrate was devoid of strychnine.

I drank 300 c. c. of the filtrate. It was not bitter, and I have not experienced any symptoms of poisoning with strychnine; and, as will be found on making the calculation, 300 c. c. of the unfiltered liquid contained about 40 milligrammes of strychnine, which is a poisonous dose. Very similar results have been obtained with a filtering material called Carferal.

Purification by Precipitation.—The only process requiring detailed remark under this heading is Clark's softening process. Waters to which this method of purification is adapted are such as contain carbonate of lime retained in solution by excess of carbonic acid. The process consists in adding lime to such waters until the excess of carbonic acid is neutralised; when this has taken place both the lime added and that in solution are precipitated as carbonate, a minute quantity remaining in solution, as carbonate of lime is not absolutely insoluble in water. By this process not only is the water softened, but a very large proportion of the organic matter contained in it is removed, and if the water be coloured, the colouring matter is also entirely or in very great part removed.

The following examples will indicate to what extent the organic matter is removed by this process :—

PARTS PER 1,000,000.

		Free. NH_3.	Albuminoid. NH_3.
I.	Before Clark's process,	0.01	0.05
	After „ „	0.01	0.02
II.	Before Clark's process,	0.025	0.22
	After „ „	0.030	0.08
III.	Before Clark's process,	0.015	0.22
	After „ „	0.020	0.07
IV.	Before Clark's process,	0.195	0.12
	After „ „	0.15	0.06

It is to be observed, that the organic matter removed can be proved to be present in the chalk precipitated.

The process presents so many advantages, and is so simple, that we are surprised not to see it in general use, and naturally expect to find on investigation that it has some great drawback. This, however, does not appear to be the case. The following objections have been raised to the process :—

1st, That the softened water attacks lead.

2d, That the process is not applicable to waters containing organic matter in large quantity, because the chalk precipitated will not subside.

3d, That as in carrying out the process on a large scale, great volumes of the water must be left at rest for many hours, extra reservoirs would be required, and the expense of water-works thereby greatly increased.

4th, That the quantity of chalk which would accumulate at the bottom of the reservoirs would require frequent removal; in short, would entail expense.

The first of these objections appears to be founded on error simply. At anyrate, it is not valid, as such softened water does not attack lead.

The second objection is to some extent true. Thus Thames water taken at London Bridge will not clear when an attempt is made to apply the Clark process to it under many days, and even then the clearance is very incomplete. But Thames water taken at Hampton Court—*i.e.*, at the place where the London water supply is taken—will clear quite well, and in a reasonable time, though perhaps not so quickly as spring water. As no one would think of taking such a water as Thames water at London Bridge as a water supply, this objection does not appear to be of much importance.

The third and fourth objections may be translated by saying, that to soften the water would cost money, a fact that no one is prepared to deny. But when we look at the infinitely more costly schemes which have been proposed for the supply of London, we are compelled to admit that the objection is really frivolous. Moreover, the engineering difficulties might, doubtless, be to a great extent got over by adopting a better system of clearing the water.

One other objection has been raised to the method—viz., that the water pipes "fur," that is, get choked up with a deposit. To this the only reply is, that softened water is now actually being supplied without this inconvenience being felt. Caterham is an instance in point.

The process is one which can be carried out in private houses. We should, perhaps, remark that the point at which enough lime water has been added is found by means of a solution of nitrate of silver. The lime water is added until a sample of the water gives a brown precipitate with the

silver solution, instead of a white or yellowish one given by the unaltered hard water. As soon as this is the case, stop the addition of lime water, and add more of the hard water, until the water no longer gives a brown colour with nitrate of silver solution.

The only other methods of purification by precipitation which have been adopted to any extent, are the addition of alum to the water, and the addition of a persalt of iron. In both cases the result is the same—viz., a precipitate is formed which carries down with it a very large proportion of the organic matter, sometimes as much as three-fourths. The Chinese, according to Sherard Osborne, use alum for the purpose of purifying the water of the river Peiho at Tien-tsin.

CHAPTER VII.

URINE AND SEWAGE.

SINCE surface wells, the water from which is often used for domestic purposes, are very liable to contamination with urine and sewage; and since, indeed, the detection of this species of contamination forms an essential part of the duty of the water-analyst, a chapter devoted to those fluids will form a not inappropriate supplement to this book.

The *urine*, as is well known, is an excretion, the composition and quantity of which are subject to great variation, according to the condition of the animal economy.

Thus, among a number of urinary analyses recorded in my own note-book, there is an instance of urine containing 4.52 grammes of solids in 100 c. c., and an instance of urine containing 1.40 grammes of solids in 100 c. c.

The latter specimen of urine had been passed shortly after drinking a quantity of beer, and illustrates a very well-known physiological fact—viz., that after drinking considerable quantities of liquids the urine becomes watery.

In like manner, the quantity of urine produced in the 24 hours is subject to variation, depending to a great extent on the needs of the animal system.

But, although specimens of urine may vary much, and although the quantities of urine excreted under particular circumstances may be very different; still the urine passed

by any hundred persons taken at random must be pretty constant both in quality and in quantity.

According to Parkes, the average quantity of urine passed by a healthy man in 24 hours is about 1500 c. c., containing 4.07 grammes of solids in every 100 c. c.s. Of these, 4.07 grammes of solids, 2.21 grammes consist of urea. Next in quantity comes the common salt; and thus urine consists chiefly of urea and common salt. In addition to the urea, urine contains some other organic substances in smaller quantities—viz., extractive matter, colouring matter, uric acid, hippuric acid, and creatinine. Besides common salt, there are likewise other mineral ingredients, such as sulphates and phosphates.

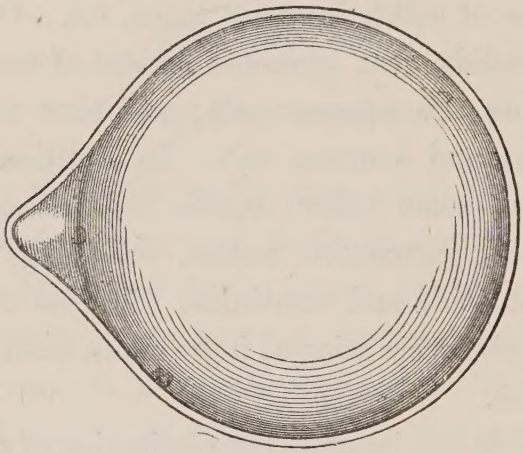
A very simple and instructive examination of urine consists in determining the total solids and the "ash." This is done as follows:—

Into a little platinum dish, which has been accurately weighed and placed in the water-bath, 5 c. c. of the sample of urine are accurately measured by means of a suitable pipette. The dish charged with the urine is then exposed to the full heat of the water-bath for two hours, and then taken out of the bath and wiped externally and weighed. The weight of the empty dish having been subtracted from the total weight of dish with urine-residue adherent to it, the difference is the weight of urine-residue yielded by 5 c. c. of urine.

After having weighed the solid residue dry at 100° cent., the next step is to ignite carefully, to cool and to weigh again, to get the ash.

These operations resemble closely the taking of solids and ash in milk (*vide* "Milk-Analysis," by J. A. Wanklyn, pub-

lished by Trübner and Co.), and require little platinum dishes weighing 12 to 14 grammes, and of the size and shape figured, also a properly-constructed copper bath, with



accurately cut holes to receive the platinum dishes, and also an accurate 5 c. c. pipette.

Very constant and accurate results are attainable in these operations, as is exemplified by the following extracts from the laboratory note-book, January 19th, 1872.

Urine passed at about 9 A.M., before breakfast, and 12 hours after taking either food or drink.

Exp. I., 5 c. c. taken and evaporated completely in the water-bath.

Dish and urine-residue	12.671	grammes.
Dish	12.483	„
	0.188	

Dish and urine-ash	12.553	grammes.
Dish	12.483	„
	0.070	

Exp. II., 5 c. c. as before.

Dish and urine-residue . . .	12.720 grammes.
Dish	12.534 „
	0.186

Dish and urine-ash	12.604 grammes.
Dish	12.534 „
	0.070

From which is deduced, in 100 c. c. of urine—

	Exp. I.	Exp. II.
Organic matter . .	2.36	2.32 grammes.
Mineral „ . .	1.40	1.40 „
	3.76	3.72

A little care is needed in the incineration, so as neither to volatilise chloride of sodium, nor to leave any serious quantity of carbon unburnt. A series of experiments, made in my own laboratory on a number of samples of urine passed by a variety of persons under a variety of circumstances, has led me to the conclusion that in health there is a certain normal ratio between the mineral constituents and the organic constituents of urine, and that during health this ratio is not widely departed from, but that in disease it is widely departed from.

Three examinations of the urine passed by the same healthy person at different dates have given results as follows:—

(Date 1871.) In 100 c. c. of urine—

Organic matter	2.96 grammes.
Mineral	1.56 „

∴ Ratio of mineral to organic = 1 : 1.90.

(Date 1871.) In 100 c. c. of urine—

Organic . . . . . 2.40 grammes.
Mineral . . . . . 1.46 „
∴ Ratio of mineral to organic = 1 : 1.64.

(Date 1872.) In 100 c. c. of urine—

Organic . . . . . 2.34 grammes.
Mineral . . . . . 1.40 „
∴ Ratio of mineral to organic = 1 : 1.67.

A different subject, also healthy, yielded urine containing in 100 c. c.—

Organic . . . . . 2.53 grammes.
Mineral . . . . . 1.50 „
∴ Ratio of mineral to organic = 1 : 1.69.

Another subject, healthy, yielded urine containing in 100 c. c.—

Organic . . . . . 2.38 grammes.
Mineral . . . . . 1.48 „
∴ Ratio of mineral to organic = 1 : 1.61.

Another healthy person, after drinking beer, yielded urine containing in 100 c. c.—

Organic . . . . . 0.80 grammes.
Mineral . . . . . 0.60 „
∴ Ratio of mineral to organic = 1 : 1.33.

This last is very instructive as exhibiting no increase in the proportion of organic matter, even when the urine has been rendered too watery by artificial means. In disease, whether merely a transient indigestion or a permanent organic lesion, the proportion of organic matter in the urine is increased, as exemplified in the following cases :—

No. 1. In 100 c. c. of urine—

Organic matter . . . . 3.31 grammes.
Mineral „ . . . . 1.49 „
∴ Ratio of mineral to organic = 1 : 2.22.

No. 2. In 100 c. c. of urine—

Organic matter . . . . 5.13 grammes.
Mineral „ . . . . 1.72 „
∴ Ratio of mineral to organic = 1 : 2.99.

No. 3. In 100 c. c. of urine—

Organic matter . . . . 2.03 grammes.
Mineral „ . . . . 0.63 „
∴ Ratio of mineral to organic = 1 : 3.22.

No. 4. In 100 c. c. of urine—

Organic matter . . . . 2.83 grammes.
Mineral „ . . . . 1.10 „
∴ Ratio of mineral to organic = 1 : 2.57.

No. 5. (diabetic urine, sugar in abundance). In 100 c. c. of urine—

Organic matter . . . . 4.42 grammes.
Mineral „ . . . . 1.68 „
∴ Ratio of mineral to organic = 1 : 2.6.

No. 6 (diabetic urine). In 100 c. c. of urine—

Organic matter . . . . 1.96 grammes.
Mineral „ . . . . 0.48 „
∴ Ratio of mineral to organic = 1 : 4.08.

These six instances comprise instances of slight derangement of health, Bright's disease and diabetes, and, as will be seen, each exhibits a far higher proportion of organic material than is present in health.

The physician is much in the habit of taking the specific gravity of urine as a guide to the condition of that excretion; but much would be gained if determinations of total solids and fixed solids were substituted for these determinations of specific gravity. The wisdom of such a substitution will be obvious when it is considered that, although specific gravities and solid contents run tolerably parallel in healthy urine, the

parallelism is lost in unhealthy urine, and it is exactly with such urine that the physician has to do.

Urea is the main solid constituent of healthy urine, and the methods of determining it will next be described.

Liebig's Method consists of a titration of the urea in urine by means of standard nitrate of mercury. The standard mercurial solution is made by dissolving either mercury, or, still better, peroxide of mercury, in excess of nitric acid, and is graduated by trial with a solution of pure urea of known strength. It is made of such a strength that one cubic centimeter exactly precipitates ten milligrammes of urea.

In using this standard solution for the determination of urea in urine, several circumstances have to be borne in mind. Sulphates and phosphates precipitate the mercurial solution, and have consequently to be got rid of before the employment of the standard solution. Chlorides, on the other hand, retard the production of the white urea-mercury compound, and have likewise to be removed as a preliminary. Albumen also possesses the property of combining with mercurial solutions, and must be removed at once before commencing the testing. Finally, it is only in solutions of a particular strength that the test works correctly, and this introduces a further complication.

The preparation of the urine is accomplished thus:—Any traces of albumen having been removed by a preliminary boiling, two volumes of the sample of urine are mixed with one volume of a baryta solution (which itself consists of two volumes of cold saturated baryta-water, mixed with one volume of cold saturated solution of nitrate of baryta), and filtered. Every 15 c. c. of filtrate contains, therefore, 10 c. c. of the urine. The chlorine in the 15 c. c. is then exactly pre-

cipitated by means of silver-solution, and the resulting chloride of silver need not be removed by filtration. To the 15 c. c. of prepared dilute urine, containing 10 c. c. of the original urine, the standard mercury solution may now be added so long as it gives a white precipitate, and until a little of the solution treated with excess of carbonate of soda on a watch-glass begins to give a brownish precipitate of peroxide of mercury. When this point has been reached, the number of cubic centimeters of standard solution must be read off. Every c. c. of mercury-solution corresponds to 0.1 gramme of urea, and, consequently, to 0.1 gramme of urea in 100 c. c. of the sample of urine. If the urine be about of normal strength—*i.e.*, a two-per-cent. solution of urea—then this titration will work accurately; otherwise, either by suitable dilution with distilled water, or else by a little correction, a result of fair accuracy may be attained.

There are also other methods of titrating urea, some of them depending on the reaction of urea on water, whereby it yields carbonic acid and ammonia.

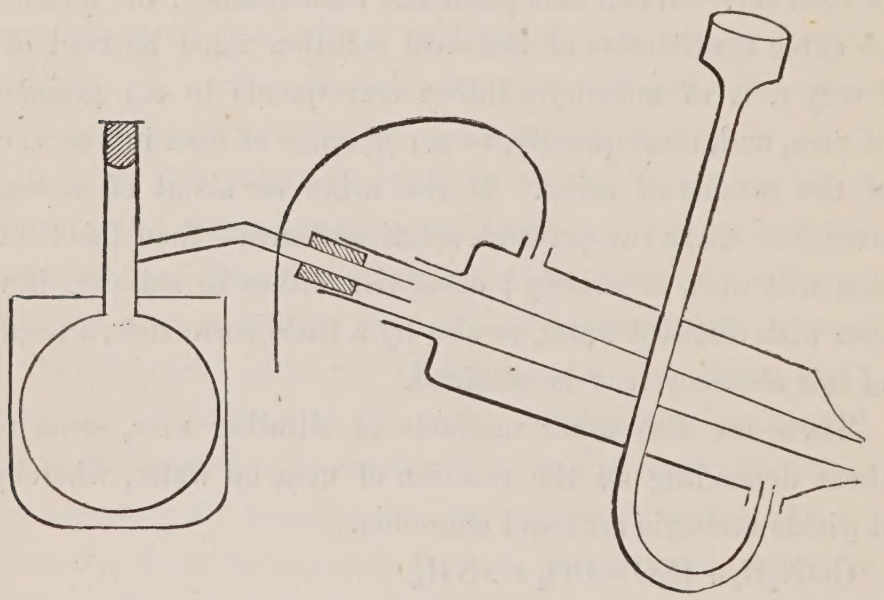
$CON_2H_4 + H_2O = CO_2 + 2NH_3$.

I have devised, and am practising, a very convenient titration of urea, the ammonia from which is *Nesslerised*. The method is the following:—

Ten cubic centimeters of a solution of caustic potash, free from all traces of ammonia (strength 10 grammes of solid potash in 100 c. c. of water), are placed in a small flask-retort (capacity about 100 c. c.), which is heated in an oil-bath. Into the potash-solution, either one cubic cent. of urine, accurately measured out, or else 10 c. c. of a one-per-cent. solution of urine, is dropped, and the whole heated to 150° Cent. in the oil or spermaceti bath, until the potash inside

the flask-retort has nearly dried up. During this operation the flask-retort is neatly connected with a small Liebig's condenser, *vide* fig.

When the contents of the flask-retort appear nearly dry—*i.e.*, when a temperature of 150° Cent. has been maintained for a short period in the interior of the flask—the temperature



should be lowered. This is done by getting the flask out of the hot oil or spermaceti, and either the oil-bath may be lowered down away from the flask, or else the flask, which is to be maintained in firm connection with the Liebig's condenser, may be raised out of the oil.

If the Liebig's condenser be held by a proper kind of clamp, made of metal lined with cork, and very firm and convenient, this raising up of the apparatus will be found to be quite easy.

In a minute or two the flask-retort will have become cool

enough to admit of the introduction of 20 c. c. of distilled water free from ammonia; and that having been done, the oil-bath is again applied to the retort, and the distillation proceeded with. This is continued almost to dryness. The resulting distillate is to be diluted with water until exactly equal to 50 c. c., and having been well stirred up, one-tenth of it (*i.e.*, 5 c. c.), or one hundredth (*i.e.*, 1 c. c.), is to be measured out and mixed with 50 c. c. of distilled water in a Nessler cylinder and Nesslerised. The result, multiplied by ten or by one hundred, gives the yield of ammonia by one cubic cent. of urine; or by $\frac{1}{10}$ c. c. of urine, if the latter quantity have been taken for the determination.

By this process I find that the yield of ammonia, from one hundred cubic centimeters of urine, is 0.90 grammes. After getting the "free ammonia," as it may be termed, it is possible, by the addition of potash and permanganate of potash, and by distillation, to get a further yield of ammonia. This, which may be called "albuminoid ammonia," amounts to 0.05 grammes per 100 c. c. of urine.

The behaviour of urea towards alkalies and towards oxidising agents in alkaline solutions is very remarkable and characteristic. Urea, when *quite* pure, may be boiled for a long time with alkalies without evolving a trace of ammonia; and even when impure, though slowly decomposed, yet the decomposition is exceedingly slow. But at temperatures some way above 100° cent., the decomposition is very rapid and complete.

In presence of permanganate and excess of potash, urea is doubtless decomposed, but it yields no ammonia, which is a very extraordinary and noteworthy fact. The property of yielding a torrent of ammonia when heated to 150° Cent. with

caustic alkali, and no ammonia at all when boiled with alkaline permanganate solution, is, I believe, quite characteristic of urea. I have, in the course of a very wide experience, never come across another substance which resembles it in this respect.

The further analysis of urine need not be entered into in this place.

Sewage.—In London each inhabitant is supplied with, on an average, at least 30 gallons of water daily. This 30 gallons of water per head, mixed with the urine and excrement, and with soap, &c., constitutes the sewage of London.

Taking the quantity of urine voided daily as 3 lbs. per head, and the water as 30 gallons (or 300 lbs.), the sewage will contain one per cent. of urine. In becoming diluted and mixed with other matters so as to form sewage, urine appears to undergo a very rapid fermentation, and yields carbonate of ammonia, so that sewage is sometimes found to be almost devoid of urea, but charged with ammonia.

Taking sewage as a solution, containing one per cent. of urine, and urine as yielding one per cent. of ammonia, sewage ought to contain 0.01 per cent. of ammonia, or 100 parts of ammonia per million. In urine there is likewise .05 per cent. of "albuminoid ammonia;" therefore, in sewage there should be 5.00 milligrammes per litre of albuminoid ammonia.

Most samples of sewage appear, however, to fall short of these quantities, and it is by no means impossible that the ureal fermentation is attended with loss of nitrogen in the form of nitrogen gas.

Harrowgate sewage, which I examined a few years ago, contained—

55.0 grains of Solids per gallon.
11.5 „ Chlorine „
The hardness was 22 degrees.

	Per million.
Free ammonia, .	55.00
Albuminoid ammonia,	3.00

PART III.

EXAMPLES

OF

COMPLETE MINERAL ANALYSES:

WATER SUPPLY TO LONDON, MANCHESTER, SUNDERLAND, AND CROYDON; THE RHINE AT BONN, AND THE WATER SUPPLY TO BONN; THE NILE.

LONDON WATER.

The main supply of water to London is in the hands of Waterworks Companies, which are, in some degree, subject to Government supervision. Rather more than half of this water is taken from the river Thames, and is purveyed by the following Waterworks Companies :—1. The West Middlesex; 2. The Grand Junction; 3. The Southwark and Vauxhall; 4. The Lambeth; 5. The Chelsea; which supply Thames water exclusively. Another company, viz., the East London Waterworks Company, draws water from both the Thames and the Lee.

The three first-named companies draw water from the Thames at Hampton; the Lambeth Company draws at Molesey; the Chelsea Company draws at Ditton; and the East London Company draws at Sunbury.

Before delivering the water to the public for general consumption, all of these companies filter it more or less completely, and with very varying success, as the examinations which I have made for a number of years have shown (*vide* page 42).

From the Government return made by Major Bolton for the month of September 1873, it appears that the average daily supply yielded by the Thames to these six companies was 65,300,014 gallons, and that that total is made up as follows :—

Daily Supply of Water from Thames during Sept. 1873.

	Gallons.
West Middlesex	9,590,863
Grand Junction	11,821,919
Southwark and Vauxhall	19,496,752
Lambeth	13,586,200
Chelsea	8,371,000
East London	2,433,280
	65,300,014

The composition of this Thames water is, no doubt, subject to some degree of variation, but in the main it is no doubt pretty constant. In the early part of April 1876, I made a complete mineral analysis of the Thames water as furnished by the West Middlesex Company, which I now publish.

	Grains per gallon.
Insoluble solids	13.2
Soluble solids	6.1
	19.3

	Grains per gallon.	
Silica	0.3	Insoluble.
Carbonate of lime	12.9	Insoluble.
Sulphate of lime	2.4	Soluble.
Sulphate of magnesia	0.6	Soluble.
Nitrate of magnesia	1.1	Soluble.
Chloride of sodium	2.0	Soluble.
	19.3	

The total lime expressed in terms of carbonate of lime amounted to 14.7 grains of $CaOCO_2$ per gallon.

The total magnesia in terms of carbonate of magnesia 1.1 grains of MgOCO per gallon.

The sulphates in terms of anhydrous sulphuric acid was 1.72 grains of SO_3 per gallon.

The direct determination of alkalies (which I regard as rather higher than the truth) gave 2.7 grains of alkaline chlorides per gallon.

The degree of alkalinity expressed in terms of carbonate of lime per gallon, could not be taken at that date. I have, however, taken it since, viz., on 13th August 1876, and find it to be 12.0 to 12.5 grains of $CaOCO_2$ per gallon, which is confirmatory of the analysis.

The river Lee, as has been said, gives water to the East London Company, which indeed takes its main supply from that river (viz., 20,222,270 gallons daily in September 1873). The New River Company takes water "from the Lee and from other sources," and in September 1873 drew from all sources at the rate of 26,602,000 gallons daily.

Towards the end of April 1876, I made a complete mineral analysis of the water furnished by the New River Company (the sample was taken in Hornsey). The following are the numbers :—

	Grains per gallon.
Insoluble solids	13.1
Soluble solids	5.9
	19.0

	Grains per gallon.	
Silica	0.26	Insoluble.
Alumina, &c.	0.14	
Carbonate of lime	12.70	
Sulphate of lime	1.60	Soluble.
Nitrate of lime	1.00	
Nitrate of magnesia	1.28	
Chloride of sodium	2·02	
	19.00	

The total lime expressed as carbonate of lime is 14.5 grains of $CaOCO_2$ per gallon.

The total magnesia is 0.76 grains of $MgOCO_2$ per gallon.

The sulphates amount to 0.93 grains of SO_3 per gallon.

The chlorides, very carefully taken, are 1.15 grains of chlorine per gallon.

The soluble residue was totally devoid of carbonates, and contained lime which was estimated.

The water supplied by the New River Company is not quite constant in composition, and it is not even quite constant all over the district.

Thus, water taken from the New River Company's main in Moorgate Street in the city, is *slightly* but *distinctly* different from water taken at the same date from the New River Company's main at Hornsey. The following are the results obtained with the samples of water from the two sources :—

	Moorgate Street Main.	Hornsey Main.
Alkalinity . . .	13.5	12.5
Hardness . . .	14.5	14.0
SO_3	0.54	0.67

These determinations were made with great care, so as to be strictly comparable. The sulphuric acid was determined in 700 c. c. of water. I have no doubt they faithfully represent a very slight but distinct difference in composition.

No doubt these differences are dependent on the circumstances of the supply being derived from different sources. On comparing together the water supplied by the Thames Companies with that from the New River Company, it will be seen that they are very similar in composition. The alkalinity, hardness, and chlorine are almost the same in

both; but the sulphates are constantly a little higher in Thames than in New River water.

The Kent Water Company differs essentially from the foregoing in being not a river-water company at all. It draws the whole of its supply from chalk wells, and, according to Major Bolton's official report for the month of September 1873, it furnished 6,749,928 gallons of water daily during that month. The company's works are situated in Deptford, Woolwich, Charlton, Plumstead, Greenwich Park, Chislehurst, Bromley, Clayford, and the Dover Road. The company does not filter, and apparently there is no need of filtration.

As has been already pointed out, the Kent Company's water is remarkably free from organic matter; but it has the disadvantage of being very hard, and very much charged with sulphates.

Analyses of the Kent water, taken at different dates, have shown that it is very constant in composition. Thus in July 1875 and August 1876 I obtained per gallon:—

	July 1875.	Aug. 1876.
Total lime expressed as carbonate of lime—grains of $CaOCO_2$ . .	20.3	20.25
Total magnesia as carbonate of magnesia—grains of $MgOCO_2$.	1.8	1.33
Total sulphates as SO_3—grains of SO	3.82	3.78

The analysis made in August 1876 was very elaborate, and the following are the particulars. The sample of water was collected at the Deptford Bridge Police Station, 21st August 1876. It gave per gallon:—

	Grains.
Insoluble solids	18.3
Soluble solids	12.0
	30.3

In this case, whilst the *total* solids were dried at 150° Cent., the soluble solids were dried at a much higher temperature; and owing to the power of sulphate of lime to retain water, it was to be expected that the analysis should exhibit a little water of hydration in the insoluble solids.

A very careful analysis of both insoluble solids and soluble solids was made, with the following results, in one gallon of Kent water:—

	Grains.	
Silica	0.75	
Alumina, &c.	0.22	
Carbonate of lime	16.30	= 18.3 Insoluble solids.
Water	1.03	
Silica, alumina, &c.	0.28	
Sulphate of lime	5.37	
Sulphate of magnesia	0.93	
Nitrate of magnesia	1.20	= 12.0 Soluble solids.
Nitrate of soda	1.21	
Chloride of sodium	2.64	
Water	0.37	
	30.30	

The analytical data are:—

From the insoluble solids:—

Silica	0.75	grains per gallon.
Alumina, &c.	0.22	„ „
$CaOCO_2$	16.30	„ „

and no magnesia.

From the soluble solids:—

Silica and alumina	0.28	grains per gallon.
$CaOCO_2$	3.95	„ „
$MgOCO_2$	1.33	„ „

The alkalies specially determined, amounted to 3.4 grains

per gallon of alkaline chlorides. Apparently a trace of potash was present.

Sulphates = 3.78 grains of SO_3 per gallon.
Chlorides = 1.75 „ Cl. „

Alkalinity, expressed as carbonate of lime, and determined by means of cochineal = 15.5 grains of $CaOCO_2$ per gallon.

The nitrates were not specially determined on this occasion, but they are pretty well known.

Fortunately for London, the Kent Company is, in point of daily supply, the smallest of the eight Water Companies from which London derives its supply of water.

As has often been pointed out, filtration renders Thames water all that can be desired for the supply of the Metropolis but no filtration can remove the objectionably high amount of sulphates from the water of the Kent Company.

In addition to the public supply of water to London, there are many private supplies by means of wells. The character of such water is very various, many of the wells being notoriously foul, and some of them yielding water of good quality.

Earlier in the book, viz., on page 48, I have given analyses of the water from the pumps in Great St. Helen's, in Bishopsgate, and in Draper's Hall. All of this water, as will be seen on turning back to the page, is very foul in character; but it would be a great mistake to conclude that this character pertains universally to London wells. There is some pure deep-spring water in the City of London.

A very elaborate investigation of London well-water has been made by the medical officer for the City of London, Dr. W. Sedgwick Saunders, to whom I am indebted for the following tabular statement of his analyses :—

ALDGATE PUMP.

Date.	Grains per Gallon. Solids.	Chlorine.	Parts per Million. Ammonia. Free.	Albuminoid.
21st May 1875 ...	... —	... 10.5	0.50	... 0.26
20th September 1875	... 88.	... 11.1	0.10	... 0.76
23d ,, ,,	... 103.	... 10.5	0.72	... 0.12
24th ,, ,,	... 108.	... 9.4	0.48	... 0.08
1st October ,,	... 111.	... 10.3	0.56	... 0.10
13th ,, ,,	... —	... 10.1	0.58	... 0.11
18th March 1876 ...	... 99.	... 10.2	0.60	... 0.12

PUMP IN BARTHOLOMEW LANE (CLOSE TO THE BANK OF ENGLAND).

18th February 1875	... 50.	... 4.1	1.40	... 0.08
21st May ,,	... —	... 4.2	2.20	... 0.10
27th September ,,	... 42.	... 4.3	1.80	... 0.08
2d ,, 1876	... 49.	... 3.8	3.88	... 0.04

WELL IN QUEEN VICTORIA STREET, CHEAPSIDE.

4th March 1876 ...	... 102.	... 9.2	2.90	... 0.44
8th ,, ,, ...	... 101.	... 9.2	3.00	... 0.24
27th April ,, ...	... 91.	... 9.3	2.75	... 0.50

WELL IN FELL STREET, CRIPPLEGATE.

31st May 1876 ...	... 123.	... 10.4	32.80	... 0.52
1st July ,, ...	... —	... —	28.40	... 0.80

The foregoing pumps and wells, which afford excellent examples of contaminated waters, have been closed by order of the medical officer. The variableness of a bad water at different dates, and according to the length of time between the taking of the samples and the analyses, is well illustrated by the above examples. A dirty water, which when freshly examined shows little "albuminoid ammonia" and much "free ammonia," is very apt to vegetate on being kept, and then shows very much albuminoid ammonia and very little free ammonia.

Omitting a number of the well waters, the analyses of which Dr. W. Sedgwick Saunders has kindly placed at my disposal, I will next quote two very instructive examples of water

which, although dubious at first sight, turned out to be uncontaminated on making a very careful investigation.

WELL AT CHRIST'S HOSPITAL.

Date.	Grains per Gallon. Solids.	Chlorine.	Parts per Million. Ammonia. Free.	Albuminoid.
25th January 1876 ...	... 75.1	... 3.4	0.10	... 0.06
14th February ,, ...	... 40.	... 2.0	0.00	... 0.05
21st ,, ,, ...	... 39.	... 1.9	0.01	... 0.06
15th September 1876	... 22.	... 1.2	0.01	... 0.03

WELL, 230 FEET DEEP, AT BLACKFRIARS.

9th June 1876 ...	... 54.	... 9.7	0.82	... 0.04
20th July ,, ...	... 57.	... 10.2	0.80	... 0.05
12th August 1876 ...	... 56.	... 10.2	0.68	... 0.02

The well at Christ's Hospital had not been pumped out when the first sample was taken, and on that account exhibited at first worse results than afterwards. The reason why the Blackfriars' well was pronounced pure was on account of the very low figure for albuminoid ammonia: and this water exhibits what is occasionally found, viz., a large quantity of free ammonia in pure deep-spring water of the first class.

MANCHESTER WATER.

Manchester is supplied with water from a gathering ground. The water is gathered on moorlands in the North of Derbyshire, and is then stored in reservoirs. The average daily supply to the town is about 14,500,000 gallons. The water is not filtered.

A sample collected in Manchester, on 24th May 1876, has given the following results on analysis :—

	Grains per gallon.
Silica	0.30
Carbonate of lime	1.70
Sulphate of magnesia	1.66
Chloride of sodium	0.91
	4.57

As will be manifest from the analysis, this water is very soft: the hardness was found experimentally to be three degrees.

It is a peaty water.

Examined by the ammonia-process, it gave—

	Parts per million.
Free ammonia	0.03
Albuminoid ammonia	0.08

Another specimen of exceedingly soft water from the moorlands in that part of the country was collected during rain by myself personally, on 10th April 1876, from a flooded stream at Holmfirth on the border of Yorkshire. The analysis gave—

	Grains per gallon.
Sulphate of lime	0.8
Sulphate of magnesia	0.6
Chloride of sodium	0.8
Nitrate of soda or potash	0.2
	2.4

This water was very peaty, and had a hardness of 3 to $3\frac{1}{2}$ degrees, a little of which was probably due to the peat.

There was considerable organic contamination.

	Parts per million.
Free ammonia	0.19
Albuminoid ammonia	0.11

SUNDERLAND WATER.

The town of Sunderland in Durham has a very extraordinary water-supply. The water is drawn from deep wells in the Dolomite, and is consequently charged with carbonate of magnesia. My analysis of a sample of this water collected at the end of March 1876 is as follows:—

	Grains per gallon.
Insoluble solids	19.2
Soluble solids	7.0
	26.2

	Grains per gallon.
Silica, &c.	0.46
Carbonate of lime	13.05
Carbonate of magnesia . . .	8.26
Sulphate of magnesia . . .	1.40
Chloride of magnesium . . .	0.50
Chloride of sodium	2.90
	26.57

The analytical data being—

		Per gallon.		
Total lime	equal to . .	13.05	grains of	$CaOCO_2$
„ magnesia	„ . .	9.46	„	$MgOCO_2$
„ alkalies	„ . .	2.9	„	NaCl
„ sulphates	„ . .	0.93	„	SO_3
„ chlorides	„ . .	2.1	„	Cl

Organically the water was very pure. It gave—

	Parts per million.
Free ammonia	0.03
Albuminoid ammonia . . .	0.02

Inasmuch as this water is so highly charged with magnesia, it affords a good example of the peculiarities of magnesian-hardness. When the degree of hardness of Sunderland water

is deliberately and efficiently observed, it is found to be more than 30 degrees. The sulphates in this water, as will be noted, are not by any means high. Expressed as anhydrous sulphuric acid, they only amount to 0.93 grains of SO_3 per gallon.

I should consider a water such as the Sunderland water not to be desirable for a general town supply.

CROYDON WATER.

In the present water supply to Croydon, in Surrey, a good example is afforded of a deep-spring water, pure organically, and at the same time unobjectionable from a mineral point of view. The town is supplied with water drawn from wells in the chalk. A sample from Waterworks yard (Croydon), July 1875, gave per gallon—

Silica	1.2 grains.
Carbonate of lime	17.8 „
Carbonate of magnesia	1.4 „
Chloride of sodium	2.0 „
Sulphate of soda	0.9 „
	23.3

The well in Mint Walk yielded, at the same date, per gallon—

Silica	1.0 grains.
Carbonate of lime	17.0 „
Carbonate of magnesia	0.7 „
Chloride of sodium	2.0 „
Sulphate of soda	0.9 „
	21.6

The nitrates were not determined in these last samples.

The Old Well at Croydon gave, in December 1875, per gallon—

Silica	trace.
Carbonate of lime	14.1 grains.
Sulphate of lime	1.8 „
Sulphate of magnesia . . .	1.4 „
Chloride of sodium	1.8 „
Nitrate of soda	1.4 „
Nitrate of potash	1.1 „
	21.6

It will be observed that the water from the wells in Waterworks yard and Mint Walk contain less sulphates than the Old Well, the numbers being 0.5, 0.5, and 1.9 grains of SO per gallon in the three waters respectively.

THE RHINE.

I have had an opportunity of making a recent examination of the water of the Rhine at Bonn.

The sample was collected by me on 3rd August 1876. It contained per gallon—

	Grains.
Insoluble solids (dry at 150° Cent.) .	9.3
Soluble solids (dry at 150° Cent.) .	4.1
	13.4

The alkalinity was 9.0 grains of $CaOCO_2$; hardness, 11.0 degrees; sulphates equal to 1.4 grains of SO_3; chlorides equal to 0.6 grains of Cl. Submitted to the ammonia-process, it gave—

	Parts per million.
Free ammonia	0.10
Albuminoid ammonia . . .	0.06

Bonn itself, as I was informed, is supplied from wells. I took a sample from a pump in the "Rheingasse" about 180 feet from the river. I found:—Total solids, 30.0 grains per gallon; hardness, 15 degrees; chlorine, 4.2 grains per gallon.

Submitted to the ammonia-process, it gave—

	Parts per million.
Free ammonia	0.22
Albuminoid ammonia	0.06

From the University pump I took water which gave—Total solids, 45.0 grains per gallon; chlorine, 8.1 grains per gallon; hardness, 21.0 degrees; and, submitted to the ammonia-process—

	Parts per million.
Free ammonia	0.00
Albuminoid ammonia	0.02

So far as I have investigated, I pronounce Bonn water to be hard, but organically pure.

THE NILE.

I have had an opportunity of making analyses of the water of the Nile, and have noticed a very interesting feature in that river.

The Nile, as is well known, is pre-eminently subject to flood, the rising of the Nile being, indeed, the chief event of the year in Egypt. Towards the end of May the Nile begins to rise, the increase in size being at first exceedingly gradual. In June the rise is just perceptible, and the river goes on increasing in volume until about the middle of September, in

which month it usually attains its greatest size. Afterwards it sinks very gradually, and about Christmas it is low. From Christmas till towards the end of May the Nile remains pretty nearly stationary in size.

The cause of the rise of the river is said to be heavy rains in the months of April and May, the effect of this rain-fall requiring the lapse of a considerable time in order to exert its full influence. Possibly, too, the melting of snow on mountains near the sources of the river may concur in flooding the river.

The height to which the Nile rises, as well as the exact period of the rise, varies from year to year, but it may be stated broadly that from the end of May until Christmas the Nile is more or less in flood, and from Christmas to the end of May the Nile is low. The following is a tabular statement of the composition of the water in different months :—

WATER OF THE NILE.

Date of sample.	Grains per gallon. Solids.	Chlorine.	Hardness.
1874 June 8 ...	15.	1.8	7.0
July 19 ...	13.	0.9	6.0
Aug. 12 ...	12.	0.3	8.5
Sept. 20 ...	10.	0.4	8.0
Oct. 12 ...	11.	0.4	7.5
Nov. 12 ...	12.	0.5	8.0
Dec. 12 ...	9.	0.45	6.5
1875 April ...	16.	1.0	8.0
May 13 ...	22.	1.2	10.0

The remarkable point brought out in this table is the great relative alteration in the proportion of chlorine, that whereas in the beginning of June, just at the beginning of the rise of the Nile, the chlorine amounts to 1.8 grains

per gallon, the chlorine sinks to 0.3 grains per gallon when the Nile has attained a great size, and remains at very little above that proportion until the end of the year.

As will be perceived, this diminution of the chlorine is proportionately very enormous, the ratio being 6 : 1. In order to be quite sure of the facts, I repeated the determination of the chlorine in the month of August, and took the precaution to evaporate down a quantity of the water to about a fifth of its volume before using the standard solution of silver. In this experiment I obtained 0.23 grains of chlorine per gallon of water. I also verified the figure 1.8 for June.

The extent of the fall in the chlorine is, therefore, quite as great as represented in the table. In marked contrast with the variableness of the chlorine, the table exhibits the comparative constancy of the hardness. On reflecting on the conditions under which the river is placed, the variableness of the chlorine and the constancy of the hardness become intelligible.

The water which swells the Nile in the latter half of the year is storm-water, being thick and muddy. Storm-water sweeps over the surface of the country, without penetrating far below the surface, and we may very readily understand that such water, passing over a country long ago denuded of salt, should carry little or no salt into the Nile, which it dilutes, and so causes to contain only an exceedingly minute proportion of chlorine.

By about Christmas, the storm-water has ceased flowing into the Nile, which, during the spring half-year, must be fed with water which has passed deeper into the ground, and which has undergone concentration by evaporation, in addi-

tion to having washed extensive strata, from which, doubtless, it extracts chlorine. We can easily understand how the Nile should become more chlorinous as the spring advances, and how the chlorine should be at the maximum just at the beginning of flood-time.

The hardness, on the other hand, being due mainly to carbonate of lime, we can understand that, from the slightness of its solubility, the carbonate of lime, and consequently the hardness, should be under totally different conditions from the chlorine.

No doubt the débris carried mechanically down with the flood-water contains abundance of finely-divided carbonate of lime, so that the storm-water must always be saturated with carbonate of lime. When in flood the Nile is, therefore, as hard as when it is not in flood, and the comparatively slight variation in hardness at different times will depend upon the varying amount of carbonic acid present in the river.

Although in the Nile the phenomena to which I have just directed attention are exhibited in a very marked manner, yet such phenomena are not confined to the Nile. If the investigation were made, I have no doubt that the Danube and the Rhine would be found to exhibit something of an analogous character, only in a far less degree; and when they are suddenly flooded, these rivers should be less charged with chlorine than at other times. The river Thames has actually been found to show analogous fluctuations in the chlorine. The importance of recognising the different causes to which fluctuation of chlorine in drinking-water is due will be obvious when it is considered how great a stress is laid upon the presence of chlorine as an index to sewage contamination.

Reverting to the Nile, I may append some determinations

of the amount of organic matter in it at different times, premising, however, that my analyses were of necessity made on water which had been kept for a considerable period of time. The results are the following :—

Date when the sample was taken from the Nile.	Parts per million. Ammonia. Free.	Albuminoid.
8th June 1874	.01	.10
10th July 1874	.04	.25
18th July 1875	.36	.28

The water of the Nile is, therefore, sometimes quite as much charged with organic matter as the Thames at Hampton Court, where the London Water Companies draw the water. But, like Thames water, it is, no doubt, amenable to wholesale filtration, and a Nile Water Company ought to deliver excellent water.

As will be observed on turning to the tabular statement above given, the water of the Nile is only about half as hard as the London Thames water. I have also to add that it is not charged to any serious extent with either magnesia or sulphates.

APPENDIX.

THE original memoirs, describing our researches into the action of oxidising agents on a great variety of organic substances in strongly alkaline solution, are reprinted from the *Journal of the Chemical Society.*

Experiments illustrative of the constancy of the ratio between the yield of albuminoid ammonia and the strength of the albuminous fluid operated upon. (*Vide Journal of the Chemical Society* for the year 1867, page 593.)

	Moist white of egg. Milligrammes employed.	Milligrammes of NH_3. Found.	Theory.
I.	17.69	0.210	0.214
II.	17.58	0.213	0.2127
III.	41.80	0.505	0.5058
IV.	27.87	0.350	0.337
V.	12.20	0.145	0.1476
VI.	7.47	0.095	0.0904
VII.	23.065	0.275	0.279

ON THE ACTION OF OXIDISING AGENTS ON ORGANIC COMPOUNDS IN PRESENCE OF EXCESS OF ALKALI.

By J. Alfred Wanklyn, Professor of Chemistry in the London Institution, and E. Theophron Chapman.

Part I. *Ammonia evolved by Alkaline Permanganate acting on Organic Nitrogenous Compounds.*

It has been observed that albumen evolves ammonia when submitted to the action of permanganate of potash in strongly alkaline solutions.* Furthermore, that this ammonia is perfectly constant in quantity, being strictly proportional to the amount of albumen employed, and that it is not the whole, but only a fraction, of the total ammonia which the total nitrogen of the albumen is capable of furnishing.†

On extending this inquiry to organic nitrogenous substances in general, we find the action of strongly alkaline permanganate to be perfectly definite, as will be apparent from the results to be given further on.

We shall confine ourselves, in this paper, to a consideration of the ammonia evolved; and in subsequent papers, in continuation of the subject, hope to render account of the residual nitrogen (when there is any), and of the other complementary products of the oxidation.

We will first describe the mode of conducting the experiments.

The ammonia evolved during the reaction was (as in the

* Wanklyn, Chapman, and Smith, *Journal of the Chem. Soc.* (1867), vol. v. [Ser. 2], 445.

† *Ibid.*, Wanklyn (1867), vol. v. [Ser. 2], 591.

papers just referred to) measured by means of the Nessler-test, and inasmuch as this test is used with very small quantities of ammonia, it was convenient to operate on very small quantities of organic matter.

In order to measure these small quantities with the necessary degree of precision, the following plan was usually adopted:—

100 milligrammes of the substance to be oxidised were weighed out and dissolved in 100 c. c. of water, thus giving a solution containing one milligramme in a cubic centimeter of the solution. By measuring this solution in an accurate burette divided into tenths of a cub. cent., or by weighing out, there was obtained the requisite quantity of the organic substance measured with the requisite degree of accuracy.

The oxidation was usually effected as follows:—Half a litre of freshly-distilled water was put into a retort, then 50 c. c. of a solution of potash (equal to ten grammes of solid potash) were added.

Then about 100 c. c. were distilled over, and usually found to be ammoniacal. This having been done, the further distillate was generally found to be ammonia-free.

Next some permanganate of potash (from 0.1 to 0.5 grm.) was added, also a few fragments of freshly-ignited tobacco-pipe (Mr. Duppa's device to avoid bumping and violent boiling).

Then the weighed or measured liquid, containing the substance to be oxidised, was put into the retort, and the distillation proceeded with.

The distillation was continued until the evolution of ammonia ceased or became very trifling.

Blank trials having been made with the distilled water and reagents, the following substances were investigated:—

I. *Asparagine*, $C_4H_8N_2O_3 + H_2O$.—The sample of asparagine

was obtained from Messrs. Hopkin and Williams, and was in beautiful crystals. It was dissolved in water.

		Milligrammes.
Substance taken	=	3.65
NH_3 obtained	=	0.80
NH_3 per cent.	=	21.92

II. *Piperine*, $C_{17}H_{19}NO_3$, from Messrs. Hopkin and Williams, was well crystallised. It was dissolved in glacial acetic acid.

		Milligrammes.
Substance taken	=	4.25
NH_3 obtained	=	0.23
NH_3 per cent.	=	5.41

III. *Chloride of Diamylamine*, $(C_5H_{11})_2H_2NCl$.—Prepared in the laboratory of the London Institution, analysed, and found to be pure.

		Milligrammes.
Substance taken	=	3.91
NH_3 obtained	=	0.31
NH_3 per cent.	=	7.93

The volatility of the substance rendered it difficult to get complete action, which accounts for the NH_3 being too low.

Diamylamine gives a white precipitate with the Nessler-test.

IV. *Amylamine*, $C_5H_{13}N$.—Prepared in the laboratory of the London Institution, by the action of iodide of amyl on ammonia. Had a perfectly constant boiling-point. Its chloro-platinate and chloride were analysed and found to be pure. It was very carefully freed from ammonia, and gave with Nessler-test a pure white (not a brownish) precipitate.

	I. Milligrms.	II. Milligrms.
Substance taken . .	2.70	1.10
NH_3 obtained . . .	0.59	0.24
NH_3 per cent. =	21.8.	NH_3 per cent. = 21.8.

V. *Diphenyl-tartramide*, $C_{16}H_{16}N_2O_4$.—Presented to us by Mr. Perkin.

	Milligrms.	Milligrms.
Substance taken	= 7.2	19.4
NH_3 obtained	= 0.70	1.98
NH_3 per cent.	= 9.72	10.21

The foregoing examples are instances of total conversion of the nitrogen of the substance into ammonia, as the following comparison shows :—

	Theory.	Found.
I. Asparagine . . .	22.66	21.92
II. Piperine . . .	5.96	5.41
III. Diamylamine Chloride .	8.79	7.93
IV. Amylamine . . .	19.54	21.8
V. Diphenyl-tartramide .	11.32	10.21

The first column of figures contains the calculated quantity of ammonia which 100 parts of the substance could give if all its nitrogen passed into ammonia. The second column gives the ammonia obtained from 100 parts of substance.

Piperidine, hippuric acid, and narcotine also give up the total nitrogen in the form of ammonia, on being boiled with strongly alkaline permanganate.

VI. *Morphine*, $C_{17}H_{19}NO_3$.—Obtained from Greville Williams, dried at 100° Cent.

	Milligrammes.
Substance taken	= 20.
NH_3 obtained	= 0.56
NH_3 per cent.	= 2.8

VII. *Codeine*, $C_{18}H_{21}NO_3H_2O$.—Splendid crystals from Macfarlane of Edinburgh.

	Milligrammes.
Substance taken	= 6.5
NH_3 obtained	= 0.195
NH_3 per cent.	= 3.00

VIII. *Papaverine*, $C_{20}H_{21}NO_4$.—From Macfarlane of Edinburgh. In good crystals.

		Milligrammes.
Substance taken	=	10.0
NH_3 obtained	=	0.22
NH_3 per cent.	=	2.2

This substance yields up the ammonia with extreme difficulty.

IX. *Strychnine*, $C_{21}H_{22}N_2O_2$.—From Messrs. Hopkin and Williams. In very good crystals, carefully dried.

		Milligrammes.
Substance taken	=	5·5
NH_3 obtained	=	0.30
NH_3 per cent.	=	5·45

X. *Iodide of Methyl-strychnine*, $C_{21}H_{22}(CH_3)N_2O_2I$.—From Dr. Crum Brown. Good crystals.

		Milligrammes.
Substance taken	=	7.2
NH_3 obtained	=	0.24
NH_3 per cent.	=	3·33

XI. *Brucine*, $C_{23}H_{26}N_2O_4$.—From Messrs. Hopkin and Williams.

		Milligrammes.
Substance taken	=	10.
NH_3 obtained	=	0.46
NH_3 per cent.	=	4.6

XII. *Sulphate of Quinine*, $(C_{20}H_{24}N_2O_2)_2H_2SO_4$.—From Messrs. Hopkin and Williams. It was carefully dried.

		Milligrammes.
Substance taken	=	10.0
NH_3 obtained	=	0.45
NH_3 per cent.	=	4·5

XIII. *Sulphate of Cinchonine*, $(C_{20}H_{24}N_2O)_2H_2SO_4$.—From

Messrs. Bullock. It was recrystallised in the laboratory of the London Institution, and dried at 100° Cent.

	Milligrms.	Milligrms.
Substance taken	= 10.00	5.00
NH_3 obtained	= 0.57	0.27
NH_3 per cent.	= 5.7	NH_3 per cent. = 5.4

These numbers (as will be apparent from the tabular statement a little further on) are somewhat in excess of the theoretical quantity for sulphate of cinchonine.

As is abundantly evident, however, from the researches which have been published on cinchonine, the formula of this substance is by no means well established. The formula just given yields 4.76 for half of the ammonia. Other formulæ which have been proposed give close on 5.00 for half of the ammonia.

XIV. *Nicotine*, $C_{10}H_{14}N_2$.—From Messrs. Hopkin and Williams.

	Milligrammes.
Substance taken	= 1.99
NH_3 obtained	= 0.215
NH_3 per cent.	= 10.80

Nicotine has no action on the Nessler-test.

XV. *Naphthylamine*, $C_{10}H_9N$.—Prepared by ourselves from nitronaphthaline. The hydrochlorate was analysed and found to be pure.

	Milligrms.	Milligrms.
Substance taken	= 12.175	4.26
NH_3 obtained	= 0.81	0.29
NH_3 per cent.	= 6.65	NH_3 per cent. = 6.81

Naphthylamine has no action on the Nessler-test.

XVI. *Toluidine*, C_7H_9N.—A well-crystallised specimen, obtained from the Continent.

	Milligrms.	Milligrms.
Substance taken	= 4.08	2.65
NH_3 obtained	= 0.36	0.22
NH_3 per cent. = 8.83		NH_3 per cent. = 8.30

Toluidine has no action on the Nessler-test.

XVII. *Acetate of Rosaniline*, $C_{20}H_{19}N_3C_2H_4O_2$.—Dried at 115° C.

	Milligrms.	Milligrms.
Substance taken	= 3.925	4.626
NH_3 obtained	= 0.25	0.30
NH_3 per cent. = 6.37		NH_3 per cent. = 6.49

In the following table, under theory, there are numbers calculated on the principle that 100 parts of the substance should give up half its nitrogen in the form of ammonia:—

	Theory. NH_3.	Found. NH_3.
VI. Morphine, ...	2.98	2.80
VII. Codeine, ...	2.67	3.00
VIII. Papaverine, ...	2.50	2.20
IX. Strychnine, ...	5.09	5.45
X. Iodide of methyl-strychnine, .	3.57	3.33
XI. Brucine, ...	4.32	4.60
XII. Sulphate of quinine, . .	4.56	4.50
XIII. Sulphate of cinchonine . .	4.76	5.7 5.4
XIV. Nicotine, ...	10.49	10.80
XV. Naphthylamine, ...	5.95	6.65 6.81
XVI. Toluidine	7.95	8.83 8.30
XVII. Acetate of Rosaniline . .	7.06	6.37 6.49

An instance of the evolution of one-third of the nitrogen in the form of ammonia, is afforded by creatine $C_4H_9N_3O_2$. The specimen of creatine taken for the experiments was kindly given to us by Mr. Greville Williams. It was dried and analysed, giving a correct result.

The mean of three accordant determinations of the ammonia evolved on boiling 100 parts with alkaline permanganate, is 12.6. The theoretical quantity, on the principle of evolution of one-third of the nitrogen as ammonia, is 12.98.

This result becomes intelligible when it is remembered that two-thirds of the nitrogen in creatine are present in the form of *urea*, and that the nitrogen of urea is evolved by alkaline permanganate, either as nitrogen gas or as nitric acid. Sarcosine, the form in which the residual third of the nitrogen is contained, will, we believe, be found to give up all its nitrogen as ammonia.

In theine we have found a substance which gives up one-fourth of the nitrogen as ammonia.

Found NH_3 from 100 parts
= 8.54
Theory = 8.76 ($\frac{1}{4}$ of the nitrogen).

The molecule of theine contains four atoms of nitrogen.

Theine, $C_8H_{10}N_4O_2$.

Uric acid also gives up a comparatively small fraction of its nitrogen in the form of ammonia.

Apparently, 100 parts of uric acid yield about 7 parts of NH_3; we shall, however, experiment further on this substance. We subjoin determinations made on substances of which the molecular weight is unknown.

100 parts of gelatine have given 12.7 parts of NH_3.

*100 parts of casein gave 7.6 parts of NH_3.

100 parts of dry albumen give about 10 parts of NH_3.

We mention, lastly, an experiment on a substance containing the whole of its nitrogen in the nitro-form, viz., picric acid,

* Of very doubtful purity.

$C_6H_2(NO_2)_3HO$. It gave no ammonia on distillation with alkaline permanganate, but yielded nitric acid, as was proved by subsequently getting abundance of ammonia on reducing the alkaline liquid by means of aluminium.

Before considering the general conclusions to be drawn from the experimental data contained in this paper, we think it useful to give a special description of the method of research which has been followed, and a discussion of some points connected with it.

The extreme minuteness of the quantities of substance subjected to quantitative determination is one of the most striking features of this investigation, and of those investigations more or less connected with it which have been published within the last year. On looking back, it will be seen that the quantity of substance taken for analysis varies from one to twenty milligrammes, being generally much nearer the former than the latter limit. In short, it may be said, without greatly exaggerating, that we have substituted milligrammes for the grammes which are ordinarily experimented on. As will have been observed, we have, accordingly, all throughout the paper given the weights in milligrammes instead of grammes.

The first point to be considered is the mode of effecting the requisite division of the substance. In one instance wherein the larger quantities were taken, as, for example, in the instance of diphenyl-tartramide, the substance was weighed on a bit of platinum foil, and employed in the solid state. In every other case the substance was employed in solution. As was described at the beginning of the paper, the usual way of proceeding was to weigh out 100 milligrammes of substance and dissolve it in 100 cub. cent. of water, or very dilute acid or alkali, according to circumstances. The dilute

solution might then, if necessary, be weighed out accurately to a milligramme, and so the substance experimented on would be capable of being divided accurately to $\frac{1}{1000}$ of a milligramme.

If ordinary care be taken, no fear need be entertained that the water used for making these dilute solutions will contain sufficient ammonia or other nitrogenous substance to vitiate the experiments. There is no great difficulty in preparing distilled water of such purity as not to give so much as $\frac{1}{100}$ milligramme of ammonia per litre. But, for making these solutions, it is not requisite to use anything better than ordinarily well-distilled water, which, made from the London water, seldom contains more than $\frac{10}{100}$ or $\frac{15}{100}$ milligramme of ammonia per litre.

Thus taking water of this quality, we will suppose 10 cub. cent. to be employed. There would be then 10 milligrammes of substance employed, and an error of $\frac{1}{1000}$ of a milligramme of ammonia introduced by reason of impurity of the water. In short, a little consideration will easily show that there is no reason for apprehending the vitiation of results in consequence of error affecting the division of the substance taken for experiment.

By a proper system of washing the apparatus, carefully cleaning out the Liebig's condenser by distilling water through it immediately before using it for an experiment on the estimation of these minute quantities of ammonia, and by carefully testing all reagents employed, it is quite easy to avoid the introduction of extraneous ammonia, and to obtain perfectly regular results.

It may be well to refer specially to the precautions to be taken in making a delicate testing of the purity of distilled water. The utmost freedom from all traces of ammonia is essential; for instance, in the case of the half-litre of water

which is destined to receive the small quantity of substance the ammonia evolved by the oxidation of which is to be estimated. In cases like this, it is not enough that 100 cub. cent. of the water should give no colouration with the Nessler-reagent, but 100 cub. cent. of the first distillate given by one litre of the water should give no reaction with the Nessler-reagent. Precise and detailed directions for the preparation and use of the Nessler-test will be found in the "Laboratory," vol. i. p. 267. To these directions we may add that we find it convenient to have our standard solution of ammonia of such a strength that one cub. cent. contains $\frac{1}{100}$ milligramme of ammonia, and that if, as sometimes happens, the Nessler-reagent should prove wanting in sensitiveness, the addition of a little solution of bichloride of mercury will render it sensitive.

Connected with the indications of the Nessler-test we have observed a point of some interest, which deserves to have attention directed to it. We have not met with any base except ammonia which gives the peculiar brownish colouration with the Nessler-reagent. Amylamine, diamylamine, and piperidine in very dilute solutions give white opalescence or precipitate when treated with the Nessler-test; naphthylamine, toluidine, and nicotine, under these circumstances occasion no reaction of any kind. (Although, however, these volatile bases cause no colouration, yet their presence more or less affects the tint which ammonia gives with the Nessler-test, and they thus, to some extent, interfere with the sharpness of the estimation of ammonia.)

There is, therefore, every reason for believing that the production of the brownish tint with the Nessler-test is quite characteristic of ammonia. The degree of precision attainable in reading the indications of the Nessler-test is much greater than would be imagined at first sight. The $\frac{5}{1000}$ of a

milligramme of NH_3 in 100 c. c. of liquid is a quantity very easily seen. The difference between $\frac{19}{100}$ and $\frac{20}{100}$ of a milligramme of NH_3 will, we think, be visible to most people. With practice a higher degree of precision is attainable. When, instead of using 100 c. c. of water for the Nessler-test, a smaller bulk is taken, the indications become more delicate. So small a quantity as $\frac{1}{1000}$ of a milligramme of ammonia may be seen in a small bulk of liquid.

In short, the Nessler-determination of ammonia is susceptible of the most wonderful delicacy.

On referring to the results given by different substances, as described in this paper, it will be seen that, putting nitro-compounds on one side, organic nitrogenous substances in general evolve ammonia on being heated to 100° C. with strongly alkaline solution of permanganates. This reaction is very general, as an inspection of the very varied list of substances contained in this paper is sufficient to show. The compound ammonias of all kinds, the amides of the acids, such substances as piperine, hippuric acid, creatine, the natural alkaloids, albumine, gelatine, and uric acid, evolve ammonia when treated in this way. Even so tough a substance as picoline, which, as is well known, is one of the most stubborn of organic compounds, yields ammonia when subjected to this treatment. Except in the instance of nitro-compounds, urea, and ferrocyanide of potassium, we have not met with any unequivocal instance of failure of an organic nitrogenous substance to evolve ammonia on being heated to 100° C. with a strongly alkaline solution of permanganate.

In the matter of the nitro-compounds, there is, be it observed, some degree of resemblance between our process and the Will and Varrentrapp process.

This difference, however, is to be noted. The Will and Varrentrapp process gives irregular results when applied to

nitro-compounds, part of the nitrogen of such compounds forming ammonia, and part not forming ammonia. Our process, on the other hand, does not convert *any* nitro-nitrogen into ammonia, but into nitric acid instead, being perfectly regular in its indications with nitro-compounds. It will be understood that, having converted the nitro-nitrogen into nitric acid, we may subsequently reduce that acid to ammonia by means of aluminium, as exemplified in the instance of picric acid above described.

On inquiring into the other peculiarities of structure which prevent alkaline permanganate evolving nitrogen of a given organic compound in the form of ammonia, our attention is arrested by the example of urea, which evolves none of its nitrogen as ammonia when so treated. The reason of this peculiarity is not far to seek, being at once visible in the formula. Urea is in a sense a perfectly oxidised substance, requiring the elements of water to transform it into carbonic acid and ammonia; and if simply oxidised, would exhibit a deficiency of hydrogen—there would be CO_{27}, and only 4H along with the N_2.

As we have seen, compounds formed by the juxtaposition of urea with another substance, with elimination of water (as, for instance, creatine, which, as is well known, is so formed from urea and sarcosine), share this property with urea, and do not give up their ureic nitrogen in the form of ammonia. Possibly uric acid furnishes so small a proportion of its nitrogen as ammonia, owing to the existence of nitrogen in the ureic state; and possibly the non-evolution of part of the nitrogen of albumen is due to the same cause.

On turning to the early part of the paper, it will be seen that whilst amylamine, diamylamine, and piperidine, substances all derived from homologues of marsh gas, undergo total conversion into ammonia, the bases toluidine, naphthy-

lamine, and nicotine, substances which are derived from hydrocarbons lower than the homologues of marsh gas, undergo only a half-conversion into ammonia. This circumstance points to the conclusion that derivation from a so-called saturated hydrocarbon implies easy conversion of the nitrogen into ammonia, whilst derivation from an unsaturated hydrocarbon interposes difficulties in the way of conversion into ammonia.

The conversion into ammonia of only half the nitrogen of so many of the natural alkaloids is an interesting fact. Some light is thrown upon it by the example of narcotine, which, although it gives up all its nitrogen as ammonia, gives it up only slowly, and by dint of putting back the distillate; it doubtless also yields parts of its nitrogen as methylamine in the first instance. A careful examination of strychnine has disclosed a somewhat similar state of matters in the case of that alkaloid. Apparently, the missing half of the nitrogen in strychnine passes provisionally into the state of some volatile alkaloid. As we said at the commencement, we reserve the treatment of the residual nitrogen for a future occasion.

NEW TESTS FOR SOME ORGANIC FLUIDS.

By J. Alfred Wanklyn, Corresponding Member of the Royal Bavarian Academy of Sciences.

In the course of the investigations connected with the establishment of the ammonia-process of water-analysis, it soon became apparent that Chapman, Smith, and myself had in our possession a new instrument of chemical research, and

in using this instrument I have, I believe, come across some very characteristic properties of the commoner animal fluids. When an animal fluid is mixed with excess of potash, evaporated down in contact with the alkali, and then maintained at a temperature of about 150° c. for some time, it evolves a certain fixed proportion of ammonia. This having been accomplished, a further quantity of ammonia may be got by boiling the residue with alkaline solution of permanganate of potash. Now, for certain animal fluids, the quantity of ammonia yielded by a given weight or volume of the animal fluid is characteristic; and the relative quantities of ammonia obtained by potash and by permanganate of potash are likewise characteristic. Thus are provided two new criteria of these animal fluids, which may become of some importance in practical biology, and especially in some of those inquiries which the medical jurist is called upon to conduct.

My investigations on this subject are far from complete, but still they are sufficiently advanced to enable some idea to be formed of the scope and possibilities of such work.

Of all the animal fluids, I know of only one which yields a large proportion of ammonia to caustic potash, and that fluid is urine. On the other hand, urine is distinguished by the smallness of the yield of ammonia to permanganate of potash.

Milk yields about half as much ammonia to potash as to permanganate of potash.

Blood yields about one-fifth as much ammonia to potash as to permanganate of potash.

White of egg, moist, just as it occurs naturally, gives about one-fourth as much ammonia to potash as to the permanganate.

Gelatine, strange to say, gives no ammonia (or only the least trace) to potash, and a good quantity to permanganate.

It is, moreover, a fact, pregnant with interest, that if the

preliminary heating to 150 c. with caustic potash be omitted, and if the boiling with permanganate be at once proceeded with, only that quantity of ammonia is obtained which would have been yielded to permanganate of potash if the entire process had been gone through. I have, in another place, insisted upon this being interpreted to mean that casein and albumen are chemical compounds into which urea enters as a constituent part, and that gelatine contains no urea.

I will next give the experimental numbers.

100 cubic centimeters give—

Name of Fluid.	Ammonia by Potash at 150° C.	Ammonia by Permanganate of Potash.
Urine (human)	0.90 gramme.	0.05 gramme.
Milk of cow	0.13 ,,	0.28 ,,
Blood of sheep	0.46 ,,	2.20 ,,
Liquid white of egg (hen) . .	0.32 ,,	1.30 ,,
Dry solid gelatine, 100 grammes.	0. gramme.	10. grammes.

These numbers must be looked upon as fair approximations, and may require a little rectification in the progress of the inquiry.

With regard to the possible applications of this work to the elucidation of questions before the medical jurist, I would suggest, just as an instance, the possibility of distinguishing between a spot of milk and a spot of white of egg on a cambric handkerchief, for these investigations are appropriately carried out on minute quantities.

In conclusion, it may, perhaps, be useful to state, that in the above experiments, 5 c. c. of the animal fluid were mixed with water in a 500 c. c. flask, and diluted up to the 500 c. c. mark, thereby forming a dilute solution, whereof 1 c. c. contained $\frac{1}{100}$ c. c. of the animal fluid; that 5 or 10 c. c. of this dilute liquid were usually taken for one experiment, and that

a delicate little retort, fitted to a delicate little Liebig's condenser, was employed. The retort was heated in an oil-bath. The ammonia was measured by the Nessler-test.

HISTORY OF THE AMMONIA-PROCESS OF WATER-ANALYSIS; AND CONTROVERSIES ON WATER-ANALYSIS.

On the 20th June 1867 I attended before a Royal Commission, which was sitting in the House of Lords and inquiring into the general question of water-supply, and gave evidence that a new process of water-analysis had been invented by myself and my colleagues, Chapman and Smith, at the same time presenting some examples of the new analyses. I also urged the objections to Dr. Frankland's process, and the Commissioners informed me that they would take care that the water-analyses for the Commission should include analyses by our new process. The Commissioners asked me whether I was on good terms with Dr. Frankland, and I replied that I was.

In the evening of the same day I read at the Chemical Society the paper on water-analysis describing the new process, and the paper was published some months afterwards in the Journal of the Society.

In the early part of the next year Dr. Frankland read a discourse on potable water to the Chemical Society, in which he attacked the ammonia-process, and described in detail the rival process of his own, viz., the combustion-process of Frankland and Armstrong. To this attack we replied, criti-

cising the rival process in the course of our reply; and both Dr. Frankland's discourse and our reply to it are to be found in the Journal of the Society for that year.

At that period, as is pretty well known, there was a strong prejudice in certain quarters against myself and my colleagues, and that very sagacious chemist, the late Dr. Mathiessen, is reported to have characterised the situation by saying that the new process had one fault, and only one, viz., that it was invented by Wanklyn, Chapman, and Smith. The reader who will take the trouble to read the blue book, with the minutes of the evidence taken at that period by the Royal Commission on water-supply, may learn what sort of an effect this prejudice had upon those persons who held chemical appointments, when they came to give evidence on water-analysis. The same blue book also contains the analyses which Drs. Frankland and Odling represented as having been made by the ammonia-process, and against which I found it my duty to protest to the Royal Commissioners.

In reference to these analyses, the remark may be made that from the dates of the analyses it is manifest that when Drs. Frankland and Odling professed to be working our process, the working details were not published. I had read our paper, but the Chemical Society had not published it, and unless Dr. Odling, who was at that time Secretary to the Society, had abused his office and used my unpublished manuscript, Drs. Frankland and Odling were not in possession of working details.

However that may be, the fact remains, that at that early period in its history, our process had to contend against a spurious set of analyses put forward officially in the name of the process, and against an official condemnation based on those spurious results. Another consequence followed on the course of action taken by Drs. Frankland and Odling—a

consequence which, though of little direct interest to chemists or the public, was of some importance to the struggling authors of the new process. Inasmuch as we were not called on by Drs. Frankland and Odling, either to co-operate with them in those analyses, or to do them ourselves for the Commission, we received none of the money which the Government paid for the working of our process; and the only course open to us was to volunteer analyses in contradiction of the spurious work for which the Commissioners were paying the public money.

Such was the posture of affairs when, in 1868, we published the first edition of the book on water-analysis, and it was in the face of these obstacles that our process has made way until, as Dr. Frankland himself said on a recent occasion, it had become "almost universally adopted."

Passing over the interval of time between 1868 and the latter part of 1875, I will next deal with the attack which, at the close of their labours in the laboratory of the late Royal Commission on the Pollution of Rivers, Dr. Frankland and his discharged assistants made on the ammonia-process.

With the article in the Brewers' Journal, and the lecture at the Society of Arts, and the various other efforts of his subordinates, I shall not trouble the reader, but shall confine myself to the efforts of Dr. Frankland himself.

On the 19th of Feb. 1876, Dr. Frankland delivered a lecture "On some Points in the Analysis of Potable Waters," and in the June number of the Chemical Society's Journal the lecture was published, and to that Journal I must request the reader to refer for amplification and verification should he desire more information than I am giving him.

Dr. Frankland begins by saying, "Eight years have now

elapsed since, in conjunction with Dr. Armstrong, I had the honour to lay before the Fellows of the Chemical Society an account of the chief determinations of water-analysis," and presently makes the assertion that the combustion-method by himself and Armstrong had been shown in his former paper to be "the only one yielding quantitative results in any degree trustworthy."

I will here pause. Although it might have been excusable in a candidate for the representation of a borough in Parliament, to assure his supporters that they were gaining the day in spite of a numerical return showing the reverse, yet the world expects a different kind of conduct from those persons who occupy high positions as scientific advisers to the Government in this country. And I invite the reader to turn to Dr. Frankland's paper of 1868, and verify the following.

In 1868 Drs. Frankland and Armstrong published ten experiments made for the express purpose of testing their combustion-method, and alleged by themselves to have established the accuracy of it. Being determined on ten litres of water, into each of which a small quantity of a known substance had been weighed, the quantities of carbon and nitrogen actually present admitted of comparison with those found by the combustion-process. These analyses show a mean average error of 0.49 milligramme in the carbon; showing in point of fact that, at that date, Drs. Frankland and Armstrong, in their so-called delicate process, made quite as large an *absolute* error as that which affects ordinary elementary analysis. I have frequently called attention to the results of 1868, and in this country they are becoming notorious, as having illustrated that the error in the Government water-analysis is as large as the total quantity pretended to be measured.

To call that showing conclusively that the combustion-process was the only one yielding quantitative results in any degree trustworthy, affords a characteristic example of the nature of Dr. Frankland's *general* statements; and taking up Dr. Frankland's own words, I would say, "In the interests of public health and for the credit of applied science," and in "the hope of attracting increased attention to accurate, as distinguished from fallacious, processes in water-analysis," I must ask the reader to follow some rather intricate details.

Dr. Frankland says that "the two chief objects to be kept in view in the analysis of potable water, are the discovery of the evidence of *past* pollution, and the quantitative determination of *present* or *actual* organic impurity."

To this I reply that the only object worth keeping in view is the present or actual impurity, and that the search for past contamination is a confession of the untrustworthiness of the test for actual contamination. At some period of its history, for anything that we can know to the contrary, any sample of water that may be brought to us may have been contaminated, and when we find a sample of water to be really pure, it is a matter of indifference whether the water had always been pure, or whether it had once been dirty, and had afterwards been purified.

Passing to the *actual* or present polluting organic matter, Dr. Frankland says, that it "can only be estimated from the amount of carbon and nitrogen found as constituents of the organic matter present in the water when the analysis is made."

In that Dr. Frankland has made another characteristic general statement: and chemists who do not know the condition of the "Chemical Society of London" may be surprised that it should be possible for one of its leaders to assert in

effect, that the only quantitative operation to which an organic substance can be submitted is the process of elementary analysis. Then Dr. Frankland tells us that his gas-apparatus can measure the one-millionth of a gramme of nitrogen, and half a millionth of a gramme of carbon. That Dr. Frankland had told the Society in 1868, when I replied that I did not doubt it, but that since his work exhibited errors of tenths of a milligramme, and a whole milligramme, his analyses were a satire on the performance of his instrument.

Then Dr. Frankland recounts his experiment of 1868, and makes the admission that the average error in the carbon is $\frac{1}{22}$ of the whole carbon taken for the experiment. He does not, however, even yet appear sensible that he is admitting that he had not attained to greater delicacy than in the ordinary combustion-process. In those experiments, wherein the experimental error was $\frac{1}{22}$ of the carbon taken, the total quantity of organic matter operated on was from .010 to .035 grammes. Chemists making common combustions, take from .100 to .400 grammes, and make an error of $\frac{1}{200}$ of the total carbon. When, therefore, Dr. Frankland had taken one-tenth of the usual quantity of organic matter, his error amounted to $\frac{1}{22}$, and therefore the absolute error remained unchanged.

Having affirmed that his method as described eight years ago was "fully equal in delicacy and certainty to all the requirements of water-analysis," Dr. Frankland proceeds to describe certain modifications, whereby he professed to have made it still more accurate, and in illustration of the degree of accuracy at length attained, published three experiments on sulphate of quinine.

The nature of these three experiments may be judged of by chemists from the following correspondence.

(FROM THE "CHEMICAL NEWS.")

To the Editor of the Chemical News.

SIR,—From the sixth and final Report of the Rivers Pollution Commission, which has recently been published, it appears that the Commissioners have not availed themselves of the modern improvements in water-analysis, but have employed the method of Frankland and Armstrong, which, as is well known, is affected with so high an experimental error as to be perfectly illusory.

The strangest peculiarity in the Report is the completeness of the demonstration of the untrustworthiness of the analytical methods employed by the Commissioners. The paper by Frankland and Armstrong, which was read to the Chemical Society in 1868, and which exhibited the experimental error of their process as being many times as great as the quantities to be measured, is republished by the Commissioners.

Methods like Frankland and Armstrong's have a tendency to yield results in accordance with the expectation of the analyst, rather than with the real composition of the sample. This characteristic (which was not prominently displayed in the paper of 1868) has been brought out in a foot-note on page 505 of the Report. I quote from this foot-note.

"Since the above was written several improvements have been made in the process. The following test experiments show that it has now (1874) attained a still greater degree of accuracy, a statement which is further corroborated by the results of very numerous series of analyses of water supplied to London, given in the diagrams facing pages 261 and 262

of this Report. To 100,000 parts of a sample of water, rendered as nearly chemically pure as possible, 1.957 part of sulphate of quinine was added. The following data compare the quantities of organic carbon and organic nitrogen thus actually added to the water with those afterwards found in the two analyses :—

	Actually Present.	Found by Analysis.	
		I.	II.
	Part.	Part.	Part.
Organic carbon in 100,000 parts of water . .	0.857	0.9120	0.904
Organic nitrogen in 100,000 parts of water . .	0.100	0.0996	0.098

"In another instance, 0.9785 part of sulphate of quinine was dissolved in 100,000 parts of water, and 0.050 part of nitrogen calculated, and 0.047, 0.048, and 0.048 found; and in a third instance 0.09785 part of sulphate of quinine taken, calculated to contain 0.005 part of nitrogen, the results of experiment being 0.006 and 0.005."

Now, by a happy mischance, Dr. Frankland's calculations of the nitrogen are miscalculations, and in the above he has afforded us an opportunity of learning by actual trial whether the result accords with the anticipation of the analyst, or with the composition of the sample.

If the reader will take the trouble to calculate the nitrogen contained by 1.957 parts of sulphate of quinine he will find it to be 0.1469, and not 0.100, as Dr. Frankland represents it. In 0.9785 part of sulphate of quinine the nitrogen is 0.0734, and in 0.09785 the nitrogen is 0.0073.

Thus we see that when 0.1469 nitrogen was really present, and when 0.100 nitrogen was supposed by Dr. Frankland to be present, his analysis exhibited a close approximation to 0.100, and similarly in the two other cases.

It would be hard to imagine a more striking exemplification of the utter worthlessness of an analytical method, and the Royal Commissioners are to be congratulated on having furnished us with it.—I am, &c.,

J. Alfred Wanklyn.

November 27, 1875.

To the Editor of the Chemical News.

Sir,—I am obliged to your correspondent for pointing out an error in a foot-note to one of the Appendices of the Sixth Report of the Rivers Commission.

The error in question is entirely an editorial one, made by myself, and has no bearing whatever upon the accuracy of the analytical results, which were obtained by Mr. W. Thorp, late chief analyst in the Laboratory of the Rivers Commission. It occurred in the following way :—The results of the experiments quoted by your correspondent were sent to me from the Rivers Commission Laboratory, by Mr. Thorp, in the following form : " 1 litre of pure water containing 0.001 grm. nitrogen as sulphate of quinine (C. = 0.008571 grm.) gave 0.000996 grm. N. and 0.00912 grm. C." In writing the article on potable water for Dr. Hofmann's " Report on the Development of the Chemical Arts during the last Ten Years," I wished to give the weights of sulphate of quinine which contained the specified quantities of nitrogen and carbon; and in calculating these weights I inadvertently used the formula $C_{20}H_{24}N_2O_2.SO_4H_2 + 7H_2O$, instead of—

$$(C_{20}H_{24}N_2O_2)_2SO_4H_2 + 7H_2O.$$

From this article the error was copied into the foot-note already alluded to.

The bottle containing the standard solution of sulphate of quinine employed in the experiments is now in my possession in this laboratory, but at the time the article was written for Dr. Hofmann it was in the Rivers Commission Laboratory in Westminster, and I could not conveniently refer to its label, from which I now copy—"Sulphate of quinine, $\frac{1}{2}$ litre = 0.7786 grm. = 0.05 grm. N. 10 c. c. = 0.001 grm. N."

The following is therefore the corrected statement of the calculated and experimental results referred to by your correspondent:—

To 100,000 parts of a sample of water rendered as nearly chemically pure as possible, 1.5572 parts of sulphate of quinine were added. The following data compare the quantities of organic carbon and organic nitrogen thus actually added to the water, with those afterwards found in two analyses:—

	Present.	Found.	
		I.	II.
Organic carbon in 100,000 parts of water . . .	0.857 part.	0.912	0.904
Organic nitrogen in do. do. .	0.100 „	0.0996	0.098

To 100,000 parts of a similar sample of water 0.7786 part of sulphate of quinine was added, and the following results obtained on analysis:—

	Present.	Found.		
		I.	II.	III.
Organic carbon in 100,000 parts of water . .	0.429 part.	0.435	0.442	0.440
Organic nitrogen in do. do.	0.050 „	0.047	0.048	0.048

To 100,000 parts of a third similar sample of pure water 0.07786 part of sulphate of quinine was added. On analysis this water yielded the following numbers:—

	Present.	Found. I.	II.	III.
Organic carbon in 100,000 parts of water . .	0.043 part.	0.047	0.050	0.055
Organic nitrogen in do. do.	0.005 „	0.006	0.005	0.006

—I am, &c.,

E. FRANKLAND.

Royal College of Chemistry, South Kensington Museum,
December 6, 1875.

To the Editor of the Chemical News.

SIR,—The letter on the Report of the above Commission which appeared in your issue of the 3rd inst. demands a reply from me.

Dr. Frankland has, I believe, written to you explaining the error which led to the insertion in the Report of the statement that "1.957 parts of sulphate of quinine" were employed, so that I need say nothing on that point, but proceed to describe the exact mode in which the experiments were made.

From his calculation that 1.957 parts of sulphate of quinine contain 0.1469 part of nitrogen, it appears that your correspondent assumes that the anhydrous salt was employed; but this was not the case, the ordinary hydrated sulphate being used. A solution was made containing in half a litre 0.7786 grm. of the salt, and 10 c. c. of this, when made up to a litre with pure water, produced a solution containing 1.5572 parts of sulphate of quinine, or 0.1 part of nitrogen in 100,000 parts. The formula which I employed was that given in Miller's "Elements of Chemistry," viz., $(C_{20}H_{24}N_2O_2)_2H_2SO + 7H_2O$, but two others have been proposed. In Watts's "Dictionary of Chemistry" $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 7\frac{1}{2}H_2O$ is given, and in Schorlemmer's "Chemistry of the Carbon Compounds"

$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$; but if either of these be taken as correct, instead of that given by Miller, the facts are not materially altered. If the salt used contained $7\frac{1}{2}H_2O$ the quantity of nitrogen in 1.5572 parts would be 0.099 part instead of 0.1 part, and if it contained $8H_2O$ it would be 0.098 part, and the numbers actually obtained in the analyses correspond still more closely with these than with the first number 0.1.

In reporting to Dr. Frankland the results of these experiments I did not state the quantity of sulphate of quinine used, but merely said that a certain quantity of nitrogen, in the form of sulphate of quinine, had been employed.

It will thus be seen that the accidental error in the Report which has given occasion to this correspondence in no way affects the accuracy of the experiments.—I am, &c.,

WILLIAM THORP, jun.,
Late Chief Assistant in the Laboratory of the Rivers Commission.

39 Sandringham Road, E.,
December 6, 1875.

To the Editor of the Chemical News.

SIR,—The following occurs on page 505 of the Appendix to the Sixth Report of the Rivers Commission :—

	Sulphate of Quinine Taken.	Nitrogen Calculated.	Nitrogen Found.
Expt. I. . .	1.95700	0.100	0.0996
Expt. II. . .	0.97850	0.050	0.0470
Expt. III. . .	0.09785	0.005	0.0060

And these quantities of sulphate of quinine do *not* contain the quantities of nitrogen which the Royal Commissioner, Dr. Frankland, thus represented them as containing. Dr. Frankland cited these experiments as establishing the validity of his process of water-analysis; and I have re-

marked that what they really do show is, that Dr. Frankland's process gives results in accordance with the expectation of the analyst, and not with the composition of the sample.

To this Dr. Frankland has made a very curious reply. He denies that he really used the above quantities of sulphate of quinine in the above experiments, and says that on reference to the label on a bottle in his possession he can now affirm that the quantities really employed were 1.5572, 0.7786, and 0.07786. He also offers some explanation of the way in which he came to say, in the Report, that he had used 1.957, 0.9785, and 0.09785. I cannot offer any suggestion as to the light in which this explanation should be viewed, and will content myself with recording it as simply as possible, only adding that Dr. Frankland's statement, that he calculated the sulphate of quinine by a wrong formula, is borne out by another reference to sulphate of quinine on page 506 of the Report, where 0.02 gramme of sulphate of quinine is affirmed to contain nitrogen equivalent to 0.00128 gramme of ammonia. In this last case the calculation (which is a miscalculation) is of very long standing, having been made by Dr. Frankland in the year 1868, and being merely reproduced in the Report of the Rivers Commission.

I have now to criticise the experiments on sulphate of quinine, assuming the correctness of the explanations given by Dr. Frankland and Mr. Thorp, who, as it would seem, made the experiments in question. The sulphate of quinine ought not to have been taken hydrated, but carefully dried. Of this Mr. Thorp appears to be partially, but only partially, sensible. He is, as his letter shows, at great pains to prove that whether hydrated sulphate of quinine contains 7, $7\frac{1}{2}$, or 8 atoms of water of crystallisation, makes no sensible difference in the percentage of nitrogen; but he altogether overlooks the difficulty which arises from the

extreme instability of the hydrated compound, which, indeed, gives up its water at ordinary temperatures if only the air in contact with it be dry. For anything that Mr. Thorp knows to the contrary, his sulphate of quinine, which he is pleased to regard as combined with some 15 per cent. of water of crystallisation, may have contained only 5 per cent. of water; and, accordingly, when he imagined he was dealing with 0.100 of organic nitrogen, and obtained experimentally 0.0996 of nitrogen, he may have been dealing with 0.110 of nitrogen. Thus, conceding to Dr. Frankland and Mr. Thorp the explanations which they have furnished after the objections to the Report of the Royal Commissioners have been pointed out to them, the sinister correspondence between expectation and result still remains, although not in so striking a form.

The extreme gravity of this "sulphate of quinine episode" may be judged of when it is considered that these experiments are the only evidence, or semblance of evidence, as yet offered by Dr. Frankland in favour of the validity of the process of water-analysis which, in his capacity of Royal Commissioner, he has employed—and employed exclusively—in the very important investigations which the Crown had commissioned him to undertake. His method of water-analysis, as is notorious, has met with general condemnation at the hands of chemists; and, with the sole exception of these experiments on sulphate of quinine, everything that he has published concerning his process has been a demonstration of its utter untrustworthiness and impracticability.—I am, &c.,

J. Alfred Wanklyn.

Dr. Frankland did not offer any further explanation; and

on 31st December 1875 the following letter appeared in the "Chemical News":—

To the Editor of the Chemical News.

Sir,—Dr. Frankland has already expressed his obligation to your correspondent for calling attention to the experiments on sulphate of quinine described on page 505 of the Appendix to the Sixth Report of the Rivers Pollution Commission. Your correspondent will now call attention to an experiment on "Fresh Urine," described on page 9 of the Report, where fresh urine is represented as containing carbon and nitrogen, in the ratio of 0.99 of carbon to 1.00 part of nitrogen. This ratio cannot be correct, inasmuch as urea (the main organic constituent of urine) contains carbon and nitrogen in the proportion of 0.43 of carbon to 1.00 part of nitrogen.—I am, &c., J. Alfred Wanklyn.

And no explanation has yet been offered by either Dr. Frankland or his assistants.

As will be noted by the reader, my letter pointing out the difficulties under which the three quinine-experiments laboured, was published on 3rd Dec. 1875, and on 19th Feb. 1876 Dr. Frankland read his discourse to the Chemical Society, and not until June was it finally published in the Journal. Why did not Dr. Frankland repeat his experiments? Dr. Frankland is not a struggling chemist, but the chemical adviser to the English Government, whose credit he has, so far as in him lies, compromised by his untrustworthy process of analysis.

Why, with the most ample means at his command, has he not provided better experimental evidence in support of his process?

After some characteristic general statements respecting his

monthly analysis for the Registrar-General (with which I shall not trouble the reader), Dr. Frankland goes on to criticise the ammonia-process. He says—"But there still remains the albuminoid-ammonia method of determining organic nitrogen. I need not describe this method, as it is well known, and is now almost as generally used by analytical chemists as were formerly the incineration and permanganate processes. This method depends upon the fact that, by boiling with an alkaline solution of potassic permanganate, most nitrogenous bodies are decomposed with evolution of ammonia. But the total nitrogen contained in organic bodies is rarely evolved as ammonia, and the proportion so evolved varies very widely when different kinds of organic matter are submitted to this reaction. The authors of the process indeed soon withdrew their statement, that albumen yielded all its nitrogen as ammonia by ebullition, first with potash, and then with alkaline solution of potassic permanganate (Journal of Chemical Society, xx. 593), nevertheless, the results yielded by this method continue to be entered in analytical tables as organic nitrogen, although its authors have never sanctioned such an interpretation."

I am fully aware that some chemists who employ the ammonia-process, do not state their results in terms of "albuminoid ammonia," which is the only correct and honest way of stating them. I could name chemists who, after analysing a water by the ammonia-process, return their results as organic nitrogen, and I heartily join Dr. Frankland in his condemnation of so dishonest a practice.

But whilst agreeing in this respect with Dr. Frankland, I must point out the misrepresentations, some of them on the surface, and others implied by the tenor of his commentary on our process.

In the first place, it is not quite correct to say that the

authors of the ammonia-process "soon withdrew their statement that albumen yielded all its nitrogen as ammonia by ebullition, first with potash, and then with alkaline potassic permanganate."

The truth is, that in our original paper of 20th June 1867, we described two modifications of the ammonia-process, one by which approximately the total nitrogen of egg-albumen was obtained as ammonia, and the other by which only a definite fraction of the nitrogen gave ammonia. In June 1867 we did not know that the two modifications gave different results, and that very remarkable peculiarity was found out by me and published later in the year. I quote the passage (Journal of the Chemical Society, xx. 593) to which Dr. Frankland refers.

"The 'albuminoid ammonia' is not the total amount of ammonia which the albumen is capable of giving, but appears to be $\frac{2}{3}$ of the total quantity, being at any rate a constant fraction of the total quantity. If, however, instead of adding permanganate of potash along with the caustic potash, or when 200 c. c. of distillate have come over the boiling with caustic potash be continued to *dryness*, then the total nitrogen, or almost the total nitrogen, in the albumen may be obtained in the shape of ammonia. This plan, which was adopted in our trial experiment referred to in the last paper, is inconvenient, and not to be recommended in practice, as it converts a very easy process into a difficult one. When we wrote the other paper we did not know that the quantities of ammonia are different in the two processes."

From this passage, written before the issue of the first edition of our water book, chemists will see that the determination of the total nitrogen did not form part of our plan of dealing with the nitrogenous substances in drinking-water. We regarded the "albuminoid ammonia" as a datum *sui*

generis, as an index to the nitrogenous organic matter at least as valuable in itself as a determination of the total nitrogen would be. Indeed, it is more valuable; inasmuch as the cases of nitro-compounds and of urea are by our process distinguished from the cases where albumen and like substances are present.

The fallacy which lurks in Dr. Frankland's commentary is, that the only quantitative operation to which organic compounds can be submitted is the process of elementary analysis into carbonic acid, water, and nitrogen.

I will answer it by a parallel. Acetic ether may be made to yield acetic acid quite quantitatively; and in whatever sense the carbon contained by acetic ether can be said to be a measure or index to the acetic ether, in that same sense the acetic acid is a measure or index to the acetic ether. An unknown mixture of acetates could not be absolutely measured by the carbon it contains, neither could the mixture be absolutely measured by the acetic acid which it gives. But in whatever sense the carbon can be said to be an approximate measure of the mixed acetates, in that same sense is the acetic acid a measure.

For acetic acid read albuminoid ammonia, for acetic ether read albuminous substances, and for mixed acetates read the miscellaneous nitrogenous organic matters in drinking-water, and the parallel is complete.

To the lecturer's objection that there are nitrogenous organic substances which yield no albuminoid ammonia, I answer that urea is the only one which is likely to occur in drinking-water, and urea is fully provided for by the ammonia-process. If, perchance, a trace of nitro-compound ever make its way into drinking-water, it would not be detected by the ammonia-process. But that is no objection to the ammonia-process, which is designed to measure the albuminoid substances and

miscellaneous nitrogenous debris in water, and which is all the more valuable for not confounding nitro-compounds with them.

Dr. Frankland winds up his discourse by summing up under four headings his objections to the ammonia-process, and under five headings the merits of the combustion-process. The foregoing is a sufficient answer to the objections.

The five points which he alleges in favour of his process are comprised by his statement No. 1, viz., That it is the only method at present known which affords any trustworthy information respecting the organic matters present in potable waters. To this I answer that, while professing to measure the carbon and nitrogen existing in organic combination in drinking-water, it fails to make such measurements, inasmuch as the organic substances are more or less decomposed and dissipated during the preliminary process of evaporation, and inasmuch as, so far as experiment has shown, the error of experiment is greater than the total quantity to be measured.

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